Analysis of Petroleum for Trace Metals

In Analysis of Petroleum for Trace Metals; Hofstader, R., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1976.

Analysis of Petroleum for Trace Metals

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Robert F. Gould, *Editor*

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

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PREFACE

The chapters in this book have been prepared from papers presented at a symposium on the "Analysis of Petroleum for Trace Metals" held at the 169th National Meeting of the American Chemical Society. The symposium reported on the Trace Metals Project carried out by five petroleum companies to develop methods for 13 elements of environmental interest (arsenic and selenium, which are not metals in the usual sense, are included). For the present purpose, the format of the papers has been changed to include detailed procedural instructions.

Each author contributed to the Project and the technical presentations at the aforementioned symposium as well as to various chapters in this book. To avoid excessive duplication, principles and techniques generally applicable to trace analysis are separated from the information and methods specific to the given elements.

Numerous analytical techniques were studied during the Project. Although most of the methods that are given in detail use some form of atomic absorption spectroscopy, other techniques were shown to be equally applicable in certain cases.

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Introduction

In 1972 an intercompany project was initiated in recognition of a need to develop techniques for measuring trace concentrations of metals in oil. At that time capabilities within the petroleum industry were limited in general to the measurement of metals at concentrations greater than 1 ppm. However, in some cases much lower concentrations of metals in petroleum had to be measured to determine whether or not petroleum products are potential causes of environmental pollution.

The Environmental Protection Agency (EPA) has listed certain elements as potentially hazardous. In accordance with the Clean Air Act Amendment of 1970, EPA set final standards for mercury and beryllium and gave priority to several other elements as potentially hazardous. In the intercompany project, 13 of these elements were studied: antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, molybdenum, nickel, selenium, and vanadium.

The objectives of the Trace Metals Project, in which the Atlantic Richfield Co., Chevron Research Co., Exxon Research and Engineering Co., Mobil Research and Development Corp., and Phillips Petroleum Co. participated, were fourfold: to define the current state of the art, to develop analytical methods for application at the part-per-billion level using techniques available at most laboratories (10 ppb, i.e., 10 ng/g, was chosen as a reasonable attainable improvement of existing technology), to determine the precision of the methods developed, and to publish the procedures and results.

Each of the laboratories contributed to the research and development of analytical methods, to cross-checking methods developed in participating laboratories, and to publication of the information which was derived. Among the areas of research and development to which the Project addressed itself were: sample preparation techniques, measurement techniques, and possibly most important of all, sources of error.

The criteria set for sample preparation techniques were that the total concentration of the element must be measured and that any necessary destruction of the petroleum matrix had to take place without loss of the constituent to be measured. In doing this, the volatility of the metal being analyzed had to be considered; for example, mercury and arsenic losses have been well documented. In choosing a method for decomposition, both the choice of material in which the decomposition

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was being carried out and the subsequent measuring step had to be considered. Using these criteria and considerations, the following decomposition techniques were studied.

- Dry ash—potential loss of elements, even those with relatively low volatility.
- Wet ash—loss of intermediate and high volatility elements.
- Digestion—high purity reagents necessary.
- Flame decomposition—applicable to only certain volatile elements.
- Bomb decomposition—applicable to only very small quantities, requires very sensitive measurement techniques.

The chemical form of the matrix in petroleum is largely unknown. Therefore, in all the procedures used, recovery had to be demonstrated by total matrix destruction (which converts the element to a common form) or by technique which is independent of form—e.g., neutron activation analysis.

The measurement techniques whose roles were considered are as follows:

- Atomic absorption spectroscopy
- Neutron activation
- Optical emission spectroscopy
- Electrochemistry
- Colorimetry
- X-ray fluorescence
- Spark source mass spectrometry.

Atomic absorption spectroscopy, which was available in most laboratories, was judged to provide sufficient sensitivity to allow it to be used to study most of the elements of interest. Neutron activation was used to study all of the elements for which it is applicable at the 10 ppb level. In the Project, this technique was used to compare data obtained by other methods and to study losses during digestions and storage. Optical emission spectroscopy was used as a screening tool for the simultaneous measurements of many elements. Electrochemistry was used where applicable as a high sensitivity technique to study contamination problems. Colorimetry was evaluated where potential application arose. X-ray fluorescence for the most part did not have the required sensitivity. Because none of the participating laboratories had their own capability in spark source mass spectrometry, the Project addressed itself to this technique only by having some analyses carried out at a commercial laboratory.

As noted, major emphasis was placed on sources of error. Throughout the entire program, the researchers had to be aware of potential contamination, volatilization, matrix effects, and interelement interfer-

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ences. Another important part of the Project was the cooperative determination of the precision of the methods that were developed. This was done within the cross-check portion of the program. Each proposed method was cross checked by at least one laboratory in addition to the initiating laboratory, in most cases, two or three. The level for cross checking was usually two to five times the detection limit. Typical petroleum and petroleum products were used to determine the applicability as well as precision and accuracy of the methods. From this phase of the work, the investigators were able to recognize problem areas and the details which had to be spelled out carefully.

The elements, the number of procedures which were developed, the detection limits, the concentration range at which the precision was measured, and the coefficient of variation are listed in Table 1.I. Figure 1.1 summarizes accuracy data for all of the methods that were developed, with ±20% limits drawn around the theoretical match line. All of the data obtained at the initiating laboratories were within the 20% limit

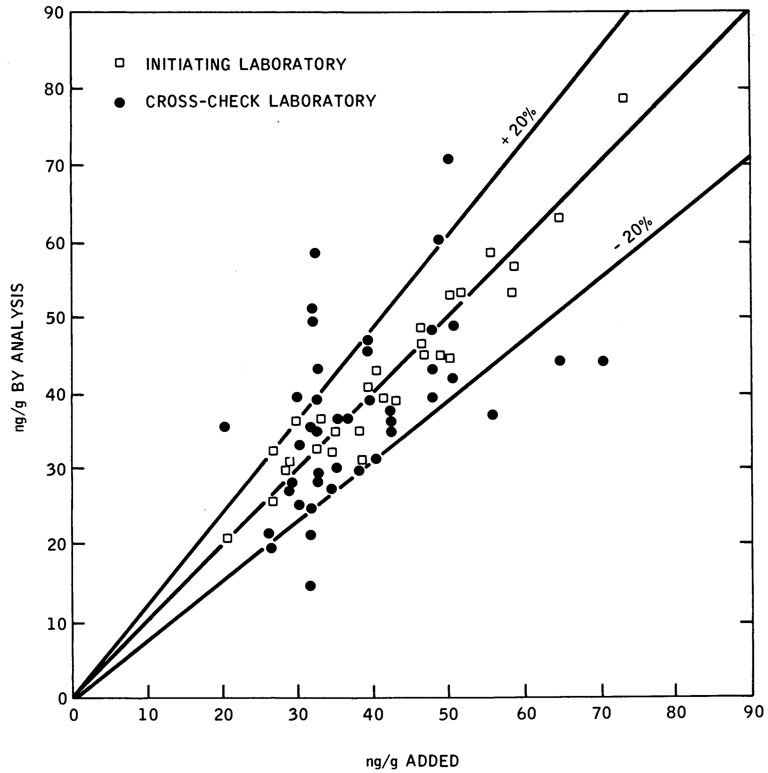

Figure 1.1. Accuracy of methods developed

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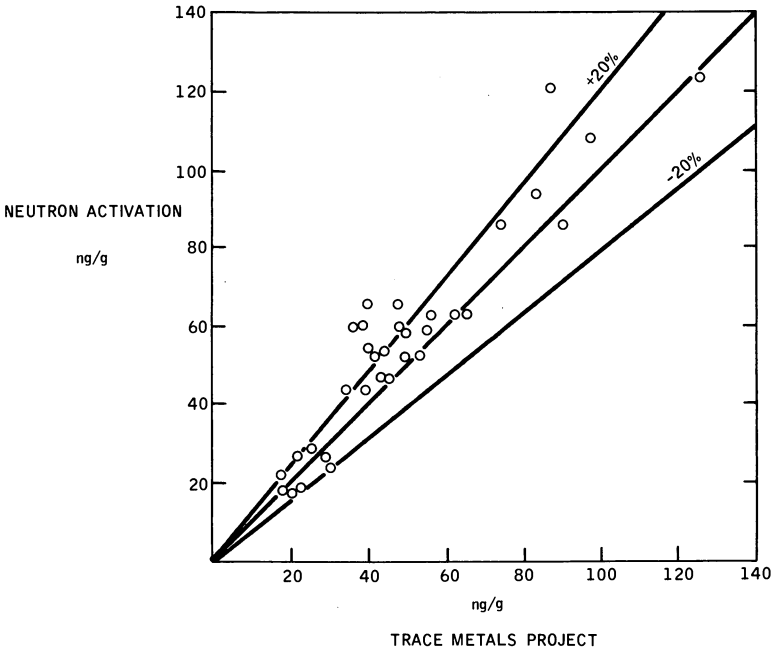

Figure 1.2. Comparison of results obtained by NAA with those obtained by trace metals project procedures

Table 1.I. Summary of Methods Developed

Element	*No. of Procedures Developed during Project*	*Detection Limit*[a] *(ng/g)*	*Concentration Level Studied (ng/g)*	*Coefficient of Variation at Level Studied*
Antimony	1	10	45	10
Arsenic	1	5	10, 100	40, 12
Beryllium	2	1	35	10
Chromium	1	10	45, 154	16
Cadmium	3	10	30	15
Cobalt	3	2	130	6
Lead	1	10	—	—
Manganese	2	10	25, 150	17, 4
Mercury	2	10	38	10
Molybdenum	2	10	25, 280	15, 4
Nickel	1	10	50, 200	16, 4
Selenium	1	10	50	20
Vanadium	1	10	40, 450	23, 3

[a] Most sensitive method.

while a small percentage of those obtained at the cooperating laboratories fell outside these limits.

Throughout the entire program neutron activation was used to cross check the data where applicable. The elements which were checked by neutron activation are: antimony, arsenic, cobalt, manganese, mercury, molybdenum, and selenium. Figure 1.2 summarizes the data obtained by both neutron activation and the procedures developed.

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Principles of Trace Analysis

> *Unless the complete history of any sample is known with certainty, the analyst is well advised not to spend his time analyzing it* (1).

Sampling

Present practice in many analytical service laboratories is to present analytical chemist with a sample and some type of formalized analysis request form. Although the analyst has no control of the sample up to this point, he is quite often the brunt of any criticism which can occur as the result of any discrepancy between his work and the "expected results." Often, little thought is given to the handling of a sample before it actually reaches the analytical laboratory. Consequently, analyses are often performed on samples which have been improperly sampled and stored, or contaminated by careless handling. Milner (2) has discussed potential and actual sources of errors associated with sampling and storage of petroleum products, the main contributor to such errors often being contamination of the sample.

Contamination can be a particularly vexing problem with regard to elemental analysis at the nanogram level. It must be remembered that anything which comes in contact with the sample, be it sampling apparatus, atmosphere, or storage container, can serve as a source of various types of elemental contamination, in amounts sometimes exceeding that of the sought-for constituent originally present. Improper sampling procedures can thus render the most stringent sample handling efforts later applied in the analytical laboratory futile.

Since the need for analytical methodology capable of determining elements at the nanogram/gram level in petroleum products has been recognized only recently, sampling procedures designed especially with regard to the unique requirements of such procedures have not yet been adequately investigated. Thus, it is not possible at this time to offer precisely defined recommendations for sampling petroleum products. It is possible, however, based on experience acquired during the course of the Trace Metals Project, to offer guidelines and general recommendations concerning sampling.

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The actual sampling process can be separated into five distinct areas for discussion.

(1) Sampling apparatus
(2) Representative sampling
(3) Storage containers
(4) Cleanliness
(5) Delay before analysis

Apparatus and procedures required for obtaining representative samples of crude petroleum and petroleum products have been developed, standardized, and documented by both American Society for Testing Materials (ASTM) and American Petroleum Institute (API) (*3, 4*). ASTM D 1265-55 (*3*) notes that judgment, skill, and sampling experience play an important role in the overall sampling process. Sampling devices described in ASTM D 270-65 (*3*) are constructed either wholly or partly from metal, and experience demonstrates that such apparatus will not contaminate the sample with the element of interest. The use of lead sheeting or uncovered lead weights to weigh down sampling bottles would obviously be questionable when procuring samples for determining trace amounts of lead. The use of metal containers with solder seams is also undesirable. It should be possible to modify or to redesign the sampling apparatus so that exposure to metal is reduced. This can be accomplished by coating the metal surfaces with inert polymeric material or substituting plastics for construction.

Fluorocarbon materials are available as laboratory equipment in a variety of shapes, sizes, and forms and are considered to provide an ideal containment and storage material. Teflon containers have been used satisfactorily by the Trace Metals Project for containing, shipping, and storing a variety of petroleum samples. Epoxy-lined metal cans and caps were also used satisfactorily for bulk storage and shipment.

The injunction given in ASTM D 270-65 (*3*) that "All sample containers must be (absolutely) clean," etc. is one which may not be easily met. Recommended procedures may not be adequate to ensure container cleaning to within an acceptable blank level. The discussion of cleaning by Adams (*5*), although directed toward glass surfaces, offers many insights into the nature of the cleaning process and should be consulted before deciding on a cleaning procedure. In addition, it is necessary to avoid concentration changes caused by surface phenomena. Such changes can be minimized by rinsing the clean container with a fraction of the sample before it is filled.

The stability of organometallic or inorganic compounds in a petroleum matrix is an important consideration in the sampling process. Stability studies on selected organometallic standards in petroleum

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matrices have been performed as a part of the Trace Metals Project and are discussed in other sections of this book.

Standards

Uses. Trace elemental analysis methods are invariably based on techniques which require standards for recovery studies as well as quantitation. The use of aqueous inorganic standards to calibrate measurements of metals in mineralized petroleum samples is well established. Such standards, however, give no information about the fate of the analyte during the critical sample preparation step. Therefore organometallic standards are required for trace element recovery studies on petroleum, regardless of whether the analysis is carried out directly or after mineralization.

Unquestionably the best material to evaluate the entire procedure is a standard sample whose composition with respect to the analyte is known exactly. The U.S. National Bureau of Standards (NBS) has undertaken the development of Standard Rerence Materials (SRM) for trace metals in gasoline and fuel oil (*6*); certified values have been established for Fe, Ni, Pb, V, and Zn in the fuel oil (SRM-1634). In addition information values (non-certified) are given for arsenic, chromium, mercury, and manganese.

In the absence of a standard sample, "spiked" samples prepared by adding a known concentration of an organometallic standard to a petroleum matrix must be used. Because the form of most native metal species in petroleum is unknown and may be variable, the Trace Metals Project investigated the availability of organometallic materials to determine those best suited for the preparation of "spiked" samples and calibration standards in petroleum at the nanogram/gram level.

Organometallic Standards. Analytical standards for petroleum analyses must be stable, soluble in a wide range of organic matrices, and compatible with other materials which might be present. Although several different groups of compounds have been suggested (*7, 8*), all are not commercially available. A comprehensive survey by NBS led to the preparation of a set of 24 compounds, mainly cyclohexanebutyrate salts or 1-phenyl-1,3-butanediono complexes, which best met the aforementioned criteria (*9*). For seven of the elements of interest to the Project, compounds are available from the NBS as Standard Reference Materials with certified metal content (Table 2.I). The same compounds are available commercially as reagent-grade chemicals without certification. For these, the supplier provides a percent metal content which is based on a calculated value for the pure compound. Other reagent chemicals, with calculated metal contents, are available for use as standards for several of

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Table 2.I. National Bureau of Standards Standard Reference Compounds for Elements of Interest to the Project

Element	*Code (SRM No.)*	*Compound*	*% Metal Certified*
Cd	1053a	cadmium cyclohexanebutyrate	24.8
Co	1055b	cobalt cyclohexanebutyrate	14.8
Hg	1064	mercuric cyclohexanebutyrate	36.2
Mn	1062a	manganous cyclohexanebutyrate	13.8
Ni	1065b	nickel cyclohexanebutyrate	13.89
Pb	1059b	lead cyclohexanebutyrate	36.65
V	1052b	bis(1-phenyl-1,3-butanediono)-oxovanadium(IV)	13.01

the elements studied. For accurate work, the metal content of these reagent chemicals must be determined by analysis.

Several organometallic standards are commercially available in solution, facilitating the preparation of standards in petroleum matrices (Angstrom, Conostan). Generally, these are metal salts of organic acids such as octoates, naphthenates, or unspecified sulfonates and are supplied in a heavy oil matrix (Angstrom, Conostan) at concentrations which range from percentages down to parts-per-million levels. Some standards are available which contain known levels of as many as 20 elements. In addition to these metal-in-oil standards, various specialty chemicals are available which may also be used once they are analyzed. Although these materials are generally sold only in bulk quantities, small portions can be obtained from some manufacturers (Tenneco-Nuodex Division, Sheppard Chemical, etc.).

Standards Selected. The standards selected for use in the Project are listed in Table 2.II. In general, organometallic sulfonates were used to take advantage of their reported superior stability and compatibility properties (*8*). In the Project, manganese and cadmium cyclohexanebutyrates (NBS) and chromium naphthenate were also used to demonstrate that recovery was independent of compound type. For selenium, a commercial metal-in-oil additive was used as the standard. Dilaurylselenide (19.0% Se) was selected because it was known to be soluble in most petroleum matrices and because it contained metal-to-carbon bonds which made it possible to evaluate better the potential losses of selenium during sample preparation. For the same reason pure organometallic compounds with carbon–metal bonds were used for antimony, arsenic, and mercury. For mercury, an additional test on the recovery was carried out by adding coal (NBS, SRM #1632), which contains mercury in a natural form, to a white oil prior to sample preparation.

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Table 2.II. Standards Studied during the Project

Element	*Standards Studied*	*Comment*
As	triphenylarsine	Used for recovery studies and standard additions Oil soluble C–As bonds
Be	Conostan-5000 Be	Used for both spiking and calibration Few alternatives available
Cd	Conostan-5000 Cd	Used for calibration and spiking
	NBS-cyclohexanebutyrate	Tested for recovery Losses noted in gasoline
Co	Conostan-5000 Co	Used for calibration and spiking
Cr	Conostan-5000 Cr	Used for calibration
	Nuodex naphthenate	Used for spiking Stable over 20 years
Hg	diphenylmercury	Used for spiking and recovery studies
	NBS-mercury in coal	Used for recovery studies C–Hg bond
Mn	NBS-cyclohexanebutyrate	Studied in comparison to sulfonate
	Conostan-5000 Mn	Used for spiking and calibration
Mo	Conostan 5000	Used for spiking and calibration
Ni	NBS-cyclohexanebutyrate	Compared with sulfonate
	Conostan-5000 Ni	Required stabilizer Used for calibration and recovery
Pb	Conostan-5000 Pb	Only preliminary recovery studies
Sb	triphenylstibine	Used for spiking and recovery Few alternatives C–Sb bonds
Se	dilaurylselenide	Used for spiking and recovery Few alternatives C–Se bond
V	Conostan-5000 V	Requires stabilizer Used for recovery and spiking

Preparation of Standards. Even when organometallic standards are available, extreme care must be used to ensure satisfactory results. Most reference materials are sold on a weight/weight basis, but dilute standards are more conveniently handled on a weight/volume basis. Consequently the first step in preparing most standards for trace analyses involves diluting a weighed amount of the reference material to a known volume with an appropriate solvent. The resulting stock standard is then diluted to the desired range. Even at the > 1000 μg/ml level, stabilizing agents may be required for some standards. For example, the NBS organometallic compounds must be heated with 2-ethylhexanoic acid and neutralized with 2-ethylhexylamine to effect solution in xylene. Similarly, Conostan provides an unspecified "stabilizer" solution which is required for preparing several standards, particularly for the transition metals Co, Mo, Ni, and V. When diluted to the nanogram/ml level, stability problems can be expected to become more severe, as illustrated in the next section. Consequently, dilute standards should be prepared just before use.

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Storage and Stability

The instability of dilute aqueous solutions is well documented. Significant losses have been observed after storage for only a few days and, in some extreme cases, within a few hours. Glass and plastic containers have been used, and several ways to stabilize solutions have been recommended. It is generally agreed that with aqueous solutions maximum stability is achieved by acidifying the solution. The optimum container material seems to depend on the specific analyte.

Concern has been expressed regarding the instability of metals in petroleum products as a potential source of error. Powers et al. (*10*) reported significant losses of natural arsenic compounds from virgin naphthas stored in steel, glass, and polyethylene containers. However, synthetic solutions of tributylarsine and triphenylarsine were stable for up to one week. The rapid losses of natural arsenic compounds were attributed to a combination of oxidation and adsorption. Agrawal and Gulati (*11*) also reported losses of arsenic from cracked and straight run naphthas stored in soft and Pyrex brand glass containers.

The Trace Metals Project conducted a study to identify the type of container which would provide minimum losses of arsenic and mercury by precipitation, volatilization, adsorption, or diffusion. Solutions of organomercury and organoarsenic compounds added to petroleum feedstock were used. Because of the relative ease with which mercury and arsenic can be determined at sub-parts-per-million levels in a hydrocarbon matrix by instrumental neutron activation analysis (INAA), this technique was used for the analytical measurements. The solutions were stored in five different types of glass and/or plastic containers and sampled periodically over eight months (*12*). The results of the study are summarized in Tables 2.III and 2.IV.

Table 2.III. **Mercury Stability Test: Hg Found (ng/g)**[a]

Time:	*0*	*1 week*	*2 months*	*3 months*	*4 months*	*8 months*
Sample Container						
polyethylene	101,90	104	101,100	102	101	98
polypropylene	95	98	98	98	100	98
Teflon	95	97	98	99	99	99
soft glass	93	93	94	101	100	99
borosilicate glass	93	97	92	104	102	100

[a] 100 ng Hg/g, added as diphenylmercury.

Table 2.IV. **Arsenic Stability Test: As Found (ng/g)**[a]

Time:	*0*	*1 week*	*2 months*	*3 months*	*4 months*	*8 months*
Sample Container						
polyethylene	112,107	108	110	106	106	95
polypropylene	109	104	103	106	97	98
Teflon	107	103	101	107	103	98
soft glass	112	106	100	99	99	99
borosilicate glass	111	112	103	106	103	102

[a] 100 ng As/g, added as triphenylarsine.

For mercury no evidence of a concentration decrease was found; however, the arsenic results showed a possible slight decrease in concentration after eight months. In neither case was there any effect which could be attributed to the type of container.

To determine the stability of natural arsenic compounds in petroleum, various crude oils which had been analyzed previously by neutron activation were reanalyzed. These crude oils were stored in glass vials and bottles. Table 2.V shows the results of this study. Two sets of analyses were made, 15 months apart, and no significant changes in the arsenic concentration were observed. This suggests that crude oils containing native arsenic can be used as reliable standards for arsenic.

One of important aspects of the Trace Metals Projects was the cross-check program of proposed analytical methods. For example, evaluation of the wet digestion flame atomic absorption method for cadmium determination (*13*) involved the preparation of petroleum samples spiked with cadmium cyclohexanebutyrate. Before these samples were shipped to cooperating laboratories, a check of the cadmium content showed unexpectedly low recoveries. To confirm this apparent loss, portions of gasoline were spiked at the 30 ng/g level with cadmium cyclohexanebutyrate and cadmium sulfonate. The samples were stored in Teflon bottles and were analyzed over a month. The results are shown

Table 2.V. Stability of Natural Arsenic Compounds in Crude Oils: As Found (ng/g)[a]

Crude Oil No.	*1971*	*1973*
1	360	430
2	280	290
3	200	220
4	170	195
5	10	10
6	230	220

[a] Estimated precision based on counting statistics is ±10%.

in Figure 2.1. The recovery from samples spiked with cadmium cyclohexanebutyrate gradually decreased over the period of study, but the added cadmium was completely recovered from samples spiked with cadmium sulfonate.

In another study, a crude oil and a kerosene were spiked with cobalt and molybdenum sulfonates at the nanogram/gram level with and without the addition of the "stabilizer" available from the supplier of these organometallics. The standard solutions were stored in Teflon bottles. Neutron activation analyses showed that they were stable in the crude oil (with or without stabilizer). In the kerosene with the stabilizer

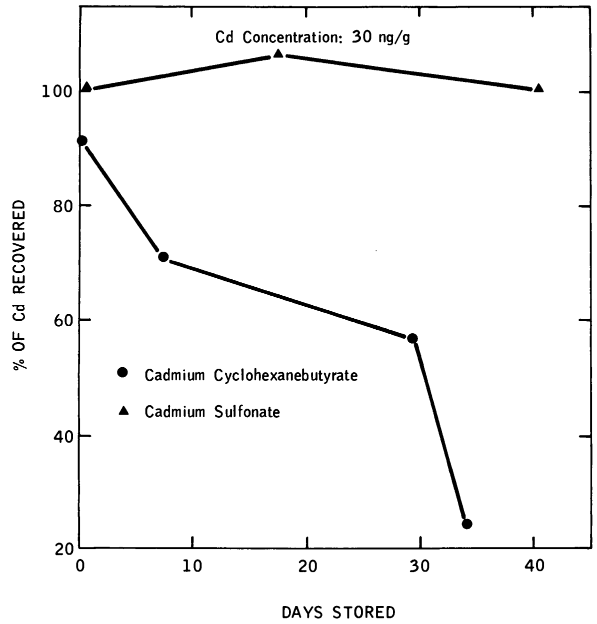

Figure 2.1. Recovery of cadmium from gasoline spiked with metalloorganic cadmium compounds

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Table 2.VI. Stability of Cobalt Sulfonates

	Co Found, ng/g			
Days after Preparation	*0*	*52*	*89*	*173*
Crude A + 100 ng Co/g	111	123	113	—
Crude A + stabilizer plus 101 ng Co/g	102	128	106	—
Kerosene + 119 ng Co/g	79	45	42	39
Kerosene + stabilizer plus 119 ng Co/g	99	127	124	—

they were stable over several months, but in the kerosene without stabilizer they deteriorated rapidly (Tables 2.VI, 2.VII). Since the nature of the organometallic, the petroleum matrix, and possibly the container affect stability, the influence of each of these factors must be established before trace metals analysis.

Contamination

The analyst is often unaware of what can and does happen to a sample between the time it reaches his laboratory and the time the actual analysis is completed. Demands for more sensitive methods of analysis have served to emphasize that all aspects of an analytical scheme must be critically examined and controlled if a meaningful analysis is to result.

Modern instrumental methods of analysis have extended the limits of detection for certain elements to the point that the detection tech-

Table 2.VII. Stability of Molybdenum Sulfonates

	Mo Found, ng/g			
Days after Preparation	*0*	*52*	*89*	*173*
Crude A + 280 ng Mo/g	280	293	275	—
Crude A + stabilizer plus 92 ng Mo/g	86	—	99	—
Kerosene + 127 ng Mo/g	—	56	48	26
Kerosene + stabilizer plus 132 ng Mo/g	152	170	117	—

nique itself no longer limits the ultimate sensitivity of an analytical method. Rather, analyses are increasingly becoming limited by the "analytical blank." Although often ignored at higher levels of concentration, the analytical blank can and does present a formidable barrier to analysis at the nanogram/gram level.

The magnitude of the analytical blank is influenced by a number of factors, both determinate and indeterminate. Murphy (*14*) has discussed the role of the analytical blank and emphasized that it is both the variability and the magnitude of the blank which ultimately determine practical lower detection limits. Efforts to develop procedures for analysis at the nanogram/gram level must therefore be directed toward minimizing those factors.

Contamination may be defined as the introduction of any compotent which can affect the numerical value finally attributed to a constituent relative to the amount present prior to sampling. Robertson (*15*) has classified contamination as follows:

(1) Positive contamination from impurities in reagents and the atmosphere or from desorption from container walls and resulting in additive errors.

(2) Negative contamination caused by losses in handling or adsorption, resulting in subtractive errors.

(3) Pseudocontamination caused by irreproducibility of experimental conditions, resulting in either positive or negative errors.

Only positive contamination is considered in detail here since it is often the most significant. Adsorption phenomena have been discussed by Adams (*5*) and by Tölg (*16*). Pseudocontamination effects can be minimized by critical evaluation and control of all aspects of the procedure.

A number of published papers discuss the effect of contamination on the analytical blank and some of the extraordinary means which are often necessary to minimize this effect. To control contamination, it is necessary to understand its sources. Basically, anything which contacts the sample between and including the actual sampling process and the completion of the analysis must be considered a potential source of contamination. These sources, along with methods used in the Trace Metals Project to minimize their effects, are summarized in Table 2.VIII.

Sources of Contamination and Ways to Reduce Its Effects. LABORATORY ATMOSPHERE. The atmosphere surrounding a sample, from the time of initial sampling to the time analysis is completed, can be a major source of contamination. Chemical laboratories, by their very nature, can be sources of virtually any element in the periodic chart and depending on geographical location and chemical history of the laboratory certain elements may be prevalent. The atmosphere in a typical laboratory, aided by heating and air-conditioning ducts and high velocity hood exhaust fans, is constantly in motion, resulting in an efficient dis-

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Table 2.VIII. Ways to Reduce High and Variable Blank Levels

1. *Laboratory Atomosphere*
    High Efficiency Particulate Air (HEPA) filtered "clean" lab located in air filtered main laboratory
2. *Reagents*
    H_2O: Double distillation of house-distilled H_2O in quartz and/or sub-boiling distillation in a quartz still
    Acids: Sub-boiling distillation in a quartz or Teflon still
    Supporting electrolytes: Long term electrolysis at a Hg-pool electrode
    Bases: High purity NH_3 vapor used for isopiestic neutralization of certain acids; produced by bubbling anhydrous NH_3 through EDTA
3. *Laboratory Ware*
    Dedicated, single purpose glassware kept in covered containers in clean room, Vycor brand vessels used whenever possible for digestions and ashing. Teflon brand products can be used where compatible with reagents, temperature, etc.
4. *Furnace Heating Elements*
    Silica furnace containing integrally molded heating elements used for digestions and ashing
5. *The Analyst*
    Teflon forceps used to handle small cells, magnetic stirring bars, etc.

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tribution of airborne contaminants. Such contamination can be either man-made or can occur from natural sources. Good laboratory housekeeping practices, combined with simple filtering of the ventilating ducts leading into a limited-access laboratory dedicated to trace analysis, can often lead to significant decreases in airborne contamination. However, because of stringent limitations on allowable limits of contamination in trace elemental analysis, it has become increasingly necessary to provide laboratory facilities having a specially controlled atmosphere referred to as "clean" or "particle-free." Such laboratories are supplied with air filtered by high efficiency particulate aid (HEPA) filters and dedicated to preparing, handling, and storing samples and reagents for ultratrace analysis. A thorough discussion of design and materials necessary for the effective implementation and utilization of controlled atmosphere facilities has been given by Paulhamus (*19*).

A "clean" laboratory based on design by Mitchell (*20*) was constructed as one aspect of the Trace Metals Project (Figure 2.2). The clean laboratory is situated in a larger main laboratory. All heating and air-conditioning ducts leading to the main laboratory are provided with coarse fiberglass filters which remove a large amount of gross airborne particulates. The clean laboratory contains a HEPA-filtered, Teflon-lined

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hood, suitable for $HClO_4$ digestions (*21*). A quartz sub-boiling distillation still (*22*) mounted in the hood is used to purify water and certain mineral acids.

Since the HEPA filters are particulate filters and will pass acid vapors, the danger of airborne metallic contamination resulting from the flaking of corroded metallic objects could exist. Thus, stainless steel fixtures were used and were coated with a Teflon spray. Other metal surfaces were covered with a protective vinyl paint. A glass-windowed exit-only emergency door was provided for safety.

Although the clean air laboratory offers the greatest advantage in eliminating contamination, other systems are available. Portable desk-top HEPA filter systems could be installed at lower cost. In addition, various ingenious apparatus and enclosures have been described (*5, 16, 18*) which allow basic processes such as heating, ashing, digestion, evaporation, etc. to be accomplished while minimizing contact with the atmosphere.

Workers often do not realize that such elaborate precautions against atmospheric contamination may be necessary since such effects could appear simply as high and variable blank levels. As part of the Project, atmospheric lead contamination was studied in a typical industrialized urban laboratory. Clean 15-ml polyethylene beakers each containing

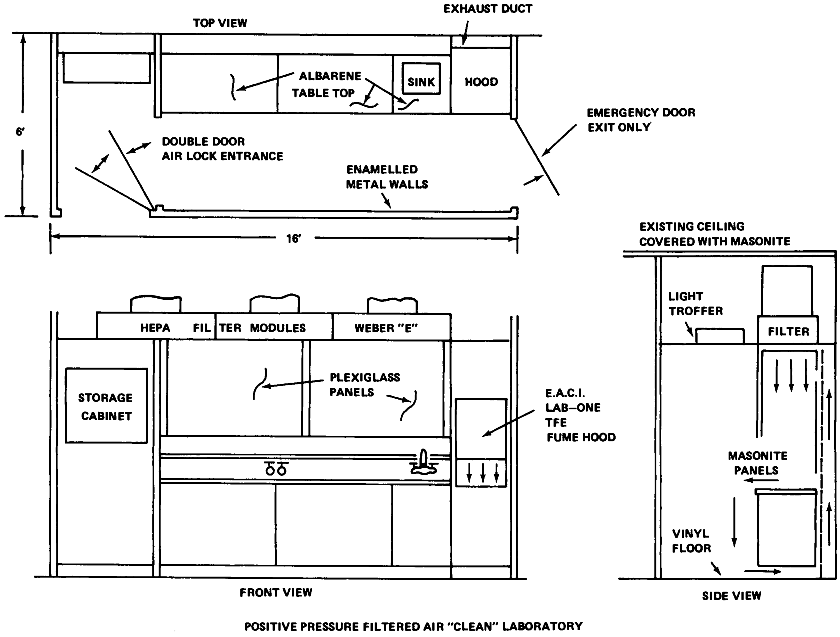

Figure 2.2. Positive pressure filtered air "clean" laboratory

1 ml of 1.5*N* HCl were placed in various locations in the laboratory, and the contents were later analyzed for lead by heated vaporization atomic absorption (Table 2.IX). Blank lead levels varied, with the highest level found for the beakers in the hood. The common laboratory hood, where most samples are prepared, is unfortunately the least desirable laboratory location in which to perform such operations from a contamination standpoint. Particulate-laden air is constantly sweeping through the hood opening, thereby greatly increasing the probability of contamination.

Table 2.IX. Effect of Laboratory Atmosphere on Lead Blank Levels

	ng Pb Found in 1 ml of Acid
Acid blank	2
Covered 2 hr on bench	1, 1.5
Uncovered 2 hr on bench	5.5, 6.2
Covered in hood 3 hr	4.5
Uncovered in hood 3 hr	25

REAGENTS. When subjected to analysis by highly sensitive instrumental techniques, even high-purity reagent-grade chemicals contain variable levels of elemental impurities. In some cases, the reagents may contain more of the sought-for element than the sample itself. Fortunately, the need for ultrahigh purity reagents has been recognized, and a whole new class of ultra- or super-pure reagents is emerging. Nevertheless, the number of commercially available ultrapure reagents, is limited. Even those reagents which are available may not be pure enough to use in some procedures. This is particularly true in wet digestion procedures where large acid/sample ratios are required. In these cases it is necessary to purify reagents in house. Zief and Barnard (*17*) have discussed some of the techniques and problems involved in preparing and storing such reagents.

Quartz sub-boiling distillation stills available in a range of prices and throughputs (*22*) can be used to purify reagents (*23*). The Teflon still described by Mattinson (*24*) is elegantly simple and can be set up easily in any laboratory. This apparatus has been used in this Project and was particularly suitable for producing small amounts of ultrapure fuming HNO_3. An apparatus for performing sub-boiling distillations enables one to prepare sufficient amounts of an acid just before use, thereby obviating some of the problems associated with storage. The choice of vessel in which to contain ultrapure chemicals is not a trivial concern, since such containers can be a major source of contamination.

Stock quantities of distilled deionized water can be prepared and stored in acid-washed carboys made from high-density polyethylene. Small amounts of this stock can be further purified by sub-boiling distil-

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lation from quartz just before use. Although high-purity water and mineral acids can be produced, the availability of high-purity bases is limited. This severely restricts the range of reactions which can be considered in developing a sample preparation procedure. High-purity NH_3 vapor, which can be used either for the isopiestic neutralization of certain acids or for preparing high-purity ammonium hydroxide, was obtained by bubbling anhydrous ammonia through EDTA solution. For electrochemical analyses, high-purity supporting electrolytes can be obtained by long-term electrolytic deposition at a mercury cathode in commercially available apparatus (*25, 26*).

GLASSWARE AND OTHER LABORATORY WARE. Since glass is not a completely inert material, its use as a container for samples must be considered carefully. Adams (*5*) has given a detailed account of the characteristics of various types of glasses and mechanisms of their interaction with solutions.

A number of problems can be avoided by careful cleaning and storage of glassware dedicated to a particular purpose. Preparation of dilute standard solutions from concentrated stock solutions just before use will minimize problems caused by instability and adsorption.

Vessels used for reagent-aided procedures are subjected to very severe conditions, first being attacked by strong acids at elevated temperatures and then subjected to even higher temperatures in a muffle furnace for long times. This Project studied blank lead levels, using several different types of commercially available ashing vessels and found Vycor brand vessels to be the best. Each vessel was washed with nitric acid, rinsed with deionized water, washed with dilute hydrochloric acid, and rinsed again before use. Of the materials studied, only a fused quartz vessel had high blanks when 1 ml of dilute acid was added cold and the vessel was rotated to wet all interior surfaces. However, when 1 ml of concentrated H_2SO_4 was evaporated, only the Vycor brand vessel maintained a low blank. Heating the Teflon beakers to temperatures sufficient to volatilize the acid caused discoloration and resulted in a lead blank level of greater than 10 ng. Lead blank levels in platinum and Pyrex beakers after heating in a muffle furnace at 450°C were also of the order of 10 ng. Vycor brand ware that becomes devitrified should be removed from service because possibilities of adsorption/desorption effects are increased.

FURNACE HEATING ELEMENTS. Ashing or heating samples in furnaces containing exposed or partially exposed heating elements can result in elemental contamination from these elements. We demonstrated this problem by using two types of muffle furnaces to study chromium contamination. One furnace had its heating elements covered with a ceramic sheet; the other was a recirculating type where air is blown over the

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heating elements and then over the sample. Blank chromium levels in the recirculating air furnace were consistently higher, indicating that the nichrome heating elements were contributing to the blank levels. Muffle furnaces can be lined with silica to reduce this effect. Furnaces constructed from foamed silica containing integrally molded heating elements have recently become commercially available (*27*). The low thermal mass and insulating properties of the silica ensure fast heating rates and good temperature stability; most important, however, these furnaces are extremely clean, with no exposed metal components.

The Analyst. The analyst is often unknowingly a source of elemental contamination. Simply touching anything which will eventually contact a sample or the analyte solution, such as a beaker, magnetic stirring bar, disposable syringe tip, etc., is enough to introduce significant quantities of some elements. Cosmetics may contribute substantial amounts of this contamination (*16*). Murphy (*14*) has cited a number of often-overlooked sources of lead contamination and has shown that lead pickup from fingers can be substantial. The anodic stripping curves shown in Figure 2.3 dramatically illustrate this effect. The stripping curve for an NH_4Cl electrolyte blank solution (a) was obtained, and the solution was found by a standard addition (b) to contain 10 ng of lead. The surface of the solution was then just touched with a finger tip, and the stripping process was repeated. The resultant curve (c) indicated that this simple process introduced gross quantities of lead as well as significant quantities of cadmium. This is a somewhat artificial example since one does not ordinarily touch reagents. It does, however, illustrate a potentially serious source of error if the cell itself is touched. A more realistic experiment was also done. The stripping curve for another blank electrolyte solution was obtained (d) and found to contain 6 ng of lead. The magnetic stirring bar used to stir the solution during deposition was removed with cleaned Teflon forceps and placed on a disposable tissue. The dry stirring bar was then picked up with the fingers and returned to the solution, and another stripping curve was obtained (e). This simple procedure introduced 7 ng of lead into the solution.

It is necessary to examine every aspect of the analytical procedure and to perform each step in an almost ritualistic manner since seemingly insignificant details can cause contamination that negates even the most careful preparation. Most of these problems can be eliminated simply. Teflon forceps should be used to handle small cells, stirring bars, or disposable syringe tips. Disposable polyethylene gloves should also be worn whenever handling larger items such as beakers, flasks, electrodes, etc. In addition, such items should be kept covered as much as possible.

Contamination can present a formidable barrier to successful analysis at the nanogram/gram level. Although heroic efforts are needed to

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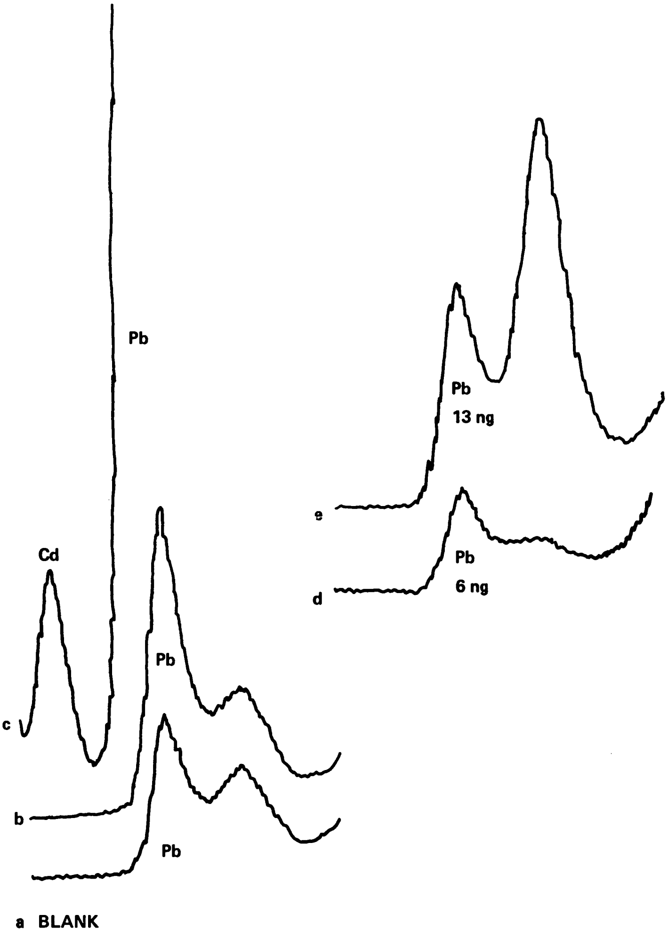

Figure 2.3. Lead contamination from fingers

combat certain types of elemental contamination, simple precautions and careful attention to experimental details are often sufficient to reduce adverse effects of contamination significantly.

Standard Additions

Petroleum matrices vary and often exert significant effects on the final measurement. This is illustrated by heated vaporization atomic absorption measurements in which various crude oils were spiked with a known concentration of an organochromium compound (Table 2.X). The data show that the absorbance is influenced by the matrix not only in the organic phase but also after the hydrocarbon has been destroyed by ashing. These differences in response indicate that the variety of

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Table 2.X. Matrix Effects in the Determination of Chromium

	Ratio Crude/Reagent Blanks (Response Factors for Added Organometallic Chromium Compound)	
	Direct	*After Ashing*
Regent blank	1.00	1.00
Crude A	1.34	1.39
B	1.21	1.25
C	0.84	1.07
D	0.43	0.98
E	0.78	1.17

crude oils behave differently not only with respect to the organic matrix but also with respect to the interelement difference. Similar effects noted for other elements are presented in their respective chapters. The technique of standard addition can be used to compensate for some of these effects.

In the technique as generally applied, increasing amounts of an analyte standard are added to aliquots of the unknown sample solution; then each aliquot is diluted to the same fixed volume. The response is extrapolated to a point on the base line concentration scale which corresponds to analyte concentration in the sample solution containing no added analyte.

The standard additions technique does not eliminate interferences; rather it compensates for the effect of this sample matrix. The use of this technique is based on the following assumptions:

(1) The standard added and the native analyte behave identically throughout the analysis.

(2) Background is nonexistent or can be corrected.

In addition, the following conditions must be met before the technique can be used satisfactorily:

(1) The technique must be applied over a concentration range where the response is linear through zero.

(2) The response must be linear in the unknown matrix.

(3) The quantity added should cause a change in the analytical response that is significant with respect to that of the sample.

In the Trace Metals Project standard additions were used in all heated vaporization atomic absorption (HVAA) procedures. These procedure's use sample aliquots of 10 μl or less; consequently, a microstandard addition technique was developed. In this technique successive microliter aliquots of a μg/ml standard are added to the sample solutions which have also been prepared on weight/volume basis. Since the volumes added or removed from the solution are negligible, the entire analysis is done on a single solution as detailed in the individual procedures.

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The concentration of the metal in the sample is calculated by one of the three following procedures:

(1) *Computation.* The metal concentration is calculated by the following equation:

$$\text{ng metal/g} = \frac{A_0 - B}{W} \times \frac{C_i}{A_i - A_o} \times F$$

where:

A_0 is the response for the sample solution
B is the background correction
i is the number of the addition (1, 2, etc.)
C_i is the total ng added after the ith addition
A_i is the response after the ith addition
W is the weight of sample in grams
F is the dilution factor (if the sample solution required dilution)

The average of three apparent concentrations of metal in the sample solution is calculated from each addition and the average is taken.

(2) *Graphical.* In this approach (which is the conventional one) the background-corrected response is plotted as the ordinate *vs.* μg/ml (or ng of metal added) and the best straight line is drawn visually through the points. The straight line is extrapolated back to intersect with the abscissa at some negative point. The point of intersection (sign neglected) gives the concentration of metal in the original sample solution.

(3) *Method of Least Squares.* In this approach the best straight line of background corrected response *vs.* μg/ml (or ng of metal added) is calculated by the method of least squares together with the standard deviation of peak heights about the regression line. Any points that lie outside 2σ of the regression line are rejected, and the regression line is recalculated.

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3

Techniques in Trace Analysis

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Sample Preparation

Most of the difficulties associated with ultratrace elemental analysis can be attributed, not to the detection step, but to the total process wherein the element of interest is removed from the sample matrix and presented to the detector system. Therefore, matrix destruction or separation and dissolution and/or concentration of the element(s) are extremely important in determining the total error in the analysis scheme. Tölg (*1*) has discussed the sources of such errors and suggested means of minimizing their effect.

Although many papers have been published describing sample preparation for biological matrices and inorganic materials, few such procedures are directly applicable to petroleum products. This is because the petroleum matrix is often extremely intractable, yielding only to the most rigorous treatment schemes. Gorsuch (*2*) has discussed organic matrix destruction in detail, and Milner (*3*) has discussed techniques particularly suitable for petroleum matrices. Some of these techniques may be quite effective for analyzing elements at the microgram/gram level or higher but may be totally unsuitable at the nanogram/gram level. This is particularly true for those techniques such as reagent-aided oxidation, wet digestion, or fusion, which require addition of reagents and which result in high reagent-to-sample ratios. Resultant elemental contamination from the added reagents is often greater than originally present.

The development of extremely sensitive instrumental detection techniques has further exposed deficiencies in sample preparation schemes presently available to the petroleum analyst. It is hoped that recognition of this situation will provide some impetus for extensive research efforts on sample preparation. During the Trace Metals Project various sample preparation schemes were investigated, some only briefly because serious deficiencies became immediately evident. The criteria set by the Project for sample preparation techniques were that for any given element the *total* concentration would be measured—i.e., any destruction of the petroleum matrix had to take place without loss of any form of the constituent to be measured.

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Table 3.I lists the techniques studied in approximate order of increasing instrumental or procedural complexity. Time limitations prevented investigation of other potentially applicable techniques. Key observations resulting from this work are:

(1) The sample preparation step can be the most critical part of an analytical procedure.

(2) No universally applicable sample preparation scheme has yet been developed; elemental characteristics often limit the choice of preparation procedures.

(3) Extensive research effort is required in virtually all aspects of the sample preparation area.

Table 3.I. Sample Preparation Techniques Suitable for Elemental Analysis at the Nanogram Level in Petroleum Products

None (direct analysis)
Dry ashing
Dilution with solvent
Reagent-aided ashing
Wet digestion or oxidation
Flame decomposition
Extraction
Bomb combustion or digestion
Oxygen plasma ashing

Direct Analysis. Analysis without prior sample preparation would be ideal since it eliminates the difficult and time-consuming task of removing or destroying the petroleum matrix and minimizes contamination. Unfortunately, at the nanogram/gram level only a few analytical techniques can be applied without prior sample preparation. These include instrumental neutron activation analysis (INAA) and heated vaporization atomic absorption (HVAA), which can be used for certain elements.

With direct HVAA, the element of interest must not be lost by volatilization or compound formation during the heating cycles. During the Project low recoveries of some elements, including Be, Ni, and Pb, were observed when using direct HVAA. In the case of Be the deficiency could be overcome.

Dry Ashing. Dry ashing possesses the advantage of simplicity in that the sample is simply heated at a high enough temperature long enough for the organic matrix to oxidize completely. For analysis at the nanogram/gram level its use is complicated by possible losses of certain elements through volatility, mechanical entrainment, or adsorption. Detailed recovery studies for a particular element and matrix must be done to verify that highly volatile elements, such as As, Hg, and Se, and moderately volatile elements, such as Cd and Pb, are not lost during ashing.

Dilution. The dilution of a sample with a solvent can be an effective way to prepare viscous samples for direct analysis, for example, by aspiration into the flame of an atomic absorption spectrophotometer or injection into an HVAA furnace. Of course, the solvent must not dilute the sample beyond the detection limits of the method or add unacceptable contamination.

Reagent-Aided Ashing. Techniques which rely on the addition of various reagents such as sulfuric or nitric acid, magnesium nitrate, sulfur, etc. either to convert the element of interest to a nonvolatile form or to help remove the carbonaceous residue have been studied. Such ashing aids must be chosen judiciously. Gorsuch (*4*) has reported the results of extensive recovery studies using radioactive tracers and various ashing aids and conditions for such elements as Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mo, Pb, Sb, Se, Sr, and Zn in organic and biological matrices. The elements were studied at the microgram/gram level or greater, and certain conditions may not necessarily be directly applicable at the nanogram/gram level. However, this work does provide a firm basis for definitive studies at the nanogram/gram level. At this level the choice of applicable ashing aids is limited to those reagents which contain a minimum amount of the sought-for element or which can be purified sufficiently.

Various reagent-aided ashing decomposition techniques were used in developing methods during the Project. They include the decomposition of large samples (20–100 g) in 500-ml Vycor beakers as well as small samples (0.5–2 g) in 50-ml Vycor crucibles. Emission spectrographic studies demonstrated that, with care, reagent-aided ashing can be used for certain elements.

A novel variation of the traditional reagent-aided ashing technique was evaluated. In this *in situ* procedure, microliter amounts of diluted samples were digested with sulfuric acid directly in a carbon cup furnace with a programmed series of drying and ashing steps just before HVAA atomization. Sample "creeping" into the optical path of the cup was a problem, however, and the technique could not be used effectively with commercially available carbon cups. In view of the minimum amount of sample handling that is required, the technique offers attractive possibilities if changes in design of the carbon cup overcome "'creeping."

Wet Digestion or Oxidation. Digestion procedures using various acids such as sulfuric, nitric, fuming nitric, perchloric, and other reagents, either alone or as mixtures, have been applied widely. The relatively low temperatures attained during the digestion tend to minimize volatilization losses, and since the sample is never taken to dryness, adsorption losses are also minimized. Contamination caused by leaching of some elements from the container walls can be significant, however, and the digestion

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vessel should be chosen accordingly. Since high reagent-to-sample ratios occur in the procedure, extremely pure reagents must be used. Fortunately, as pointed out on p. 18, mineral acids can be readily purified by sub-boiling distillation (*5*). However, the final digestate, usually a strong acid solution, may not be amenable to direct analysis by a particular technique—e.g., anodic stripping voltammetry.

Flame Decomposition. Utilization of a petroleum sample as a fuel for combustion in a specially devised burner system, such as that described by Wickbold (*6*), can be an effective way to destroy large amounts of an organic matrix. The method is applicable to those elements which are either volatile or form volatile compounds and which can be trapped quantitatively in a suitable scrubber. This technique was used to prepare samples for cold vapor atomic absorption determination of mercury. Details are included in Chapter 12.

Extraction. A completely different approach is that in which the element is removed and concentrated by extraction from the matrix. Large sample-to-extractant ratios can be utilized, thus reducing contamination. Because of the complex nature of petroleum, total recovery on samples containing naturally occurring elements should be confirmed before using an extraction technique. This can be done by comparing the extraction results with those obtained by independent techniques utilizing total decomposition.

In the Project, extraction procedures using "scavengers" were investigated. Arsenic compounds can be removed from petroleum distillates by adsorption on silica gel. Raney nickel can be used as a scavenger for arsenic in light hydrocarbons and for selenium in aqueous solutions. When Raney nickel scavenging was used for crude oils, however, incomplete recoveries were obtained. Because of potential limitations and limited elemental applicability, scavenging techniques were not investigated further.

Oxygen Bomb Combustion. This technique can oxidize organic matter quickly and completely and was therefore extensively investigated during the Trace Metals Project. The result demonstrated that oxygen combustion bombs, at least as presently constructed, are unsuitable for use at the nanogram level for the elements of interest to the Project. Initial studies, in which mineral oil spiked with 11 elements at the 100-μg/g level was decomposed in a commercially available stainless steel bomb, confirmed that the sample could be completely oxidized. Various acids were used to dissolve the residue. Analysis of the dissolved residue resulted in high recoveries for most elements, indicating contamination from the bomb walls. The bomb was modified by replacing the standard nickel sample cup with a platinum cup and by placing a glass liner in the bomb. With this equipment, recoveries for Cd, Mn, and Mo were essentially quantitative, but for the other elements recoveries were either erratic or greater than 100%. Additional studies were made by oxidizing white oil samples spiked at the sub-microgram level with various elements in a platinum-lined bomb. Except for Cr and Ni, which were high because of contamination, recoveries for most elements were low, suggesting incomplete dissolution of the residue. Because of the prohibitively high price of this bomb and the possibility of causing it irreparable damage, exhaustive dissolution studies were not conducted.

A gold-lined bomb was studied for use in preparing samples for boron determination. White oil spiked with boron sulfonate yielded high recoveries, indicating contamination.

Recently, decomposition vessels have become available which consist either of a Teflon sample container enclosed in a stainless steel jacket (*7*, *8*) or which are constructed entirely of Teflon(*9*). The steel-jacketed cells can be used at higher temperatures and pressures than the all-Teflon cells but are subject to contamination from the jacket. In any case, the amount of sample should be chosen to avoid the possibility of developing excess pressure.

Although designed primarily for decomposition of inorganic materials, all-Teflon cells can be used for decomposing small amounts ($\leqq 500$ mg) of biological materials. Petroleum matrices are not easily decomposed because of temperature restrictions and types of acids which can be used. The all-Teflon vessels have been used for pressurized acid solubilization and partial decomposition (in effect a pressurized reagent-aided pre-ash) prior to ashing in a muffle furnace. Fuming nitric acid has been particularly useful in this system.

Low Temperature Oxygen Plasma Ashing. Low temperature ashing with a radiofrequency generated oxygen plasma possesses a number of unique features which could qualify it as an ideal preparation scheme. It has, in fact, been used successfully for a number of organic and biological matrices, using commercially available equipment (*10*). Applications to petroleum products have not been particularly successful. Decomposition times for heavy petroleum fractions are often measured in days rather than hours, thereby increasing the possibility of contamination and volatility losses (reduced pressures are required to maintain the plasma) and necessitating the use of extremely pure oxygen. Kaiser et al. (*11*) described a system utilizing a 2450-MHz excited plasma which was applied to a wide variety of biological matrices. Nanogram amounts of both volatile and nonvolatile elements could be recovered with yields greater than 98%, although a liquid nitrogen cooled receiver trap was required for complete recovery of volatile elements. Ashing times were also greatly reduced, presumably because the quartz cell containing the sample was placed directly in the resonant cavity so that the oxygen

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Advances in Chemistry; American Chemical Society: Washington, DC, 1976.

plasma could impinge directly on the sample. The major disadvantage of the technique is that samples must be processed singly, thus severely restricting sample throughput.

In the Project, oxygen plasma ashing techniques, with an apparatus similar to that described by Kaiser and a commercially available induction furnace (*12*), were investigated as sources of oxygen plasma. Although time limitations restricted this work, some qualitative observations were made. Ashing times for various petroleum matrices were considerably shortened if the oxygen pressure was relatively high. Difficulties in maintaining the 2450-MHz generated plasma at higher pressures were experienced, however, thereby obviating any advantage of shorter ashing times. A 12.5-MHz generated oxygen plasma could be maintained at higher pressures, and ashing times for various petroleum samples (100–500 mg) varied from tens of minutes to several hours. Dramatic changes in ashing times were observed simply by changing such variables as oxygen flow rate, geometry of flow, surface area of sample, and cell geometry. Additional experiments must be carried out, however, before a practical system can be defined.

Flame Atomic Absorption

Since flame atomic absorption (FAA) has been described thoroughly elsewhere, only a brief discussion is given here. In general, FAA utilizes an experimental arrangement such as that shown in Figure 3.1 in simplified form. The radiation from a modulated hollow cathode lamp, whose cathode is made from the element of interest, is passed through a flame into which the sample solution is sprayed, and thence into a monochromator where the resonance line is isolated. The absorption of that line by the atoms in the flame is detected by a photomultiplier, and the signal is demodulated, amplified, and recorded. The relationship between

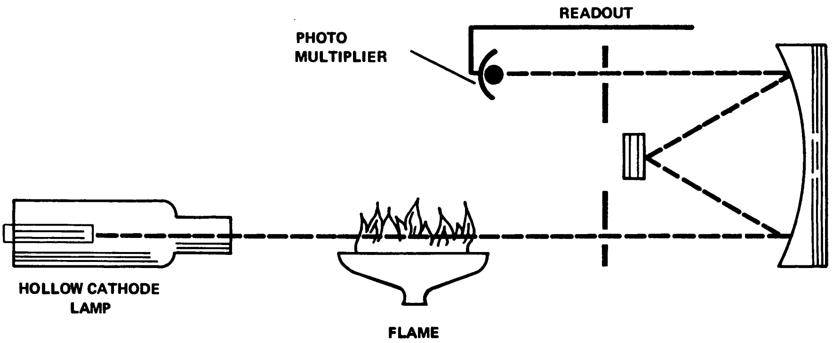

Figure 3.1. Atomic absorption apparatus (simplified)

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the observed absorption and the concentration of analyte in the solution is established by one of several calibration techniques.

Capabilities and Restrictions. The characteristics of flame atomic absorption generally make it attractive for trace metals analyses in dilute solution, but in more complex matrices the technique is limited. For most of the elements of interest to the Project, FAA has exceptional selectivity and high sensitivity. In addition, data may be collected rapidly on a wide variety of elements with comparatively low cost instrumentation. In complex matrices, chemical interferences, matrix effects, and background absorption all require the development of special techniques. Chemical interferences are generally eliminated by using releasing agents and high temperature flames. Matrix effects, such as viscosity, may require the development of special compensation techniques based on matrix matching. Standard additions procedures may be used to correct for both effects. Correlations for background (continuum) absorption caused by entrained particles or incomplete combustion products must be carried out either by a sequential background measurement at a "non-absorbing" line or by a simultaneous electronic correction based on attenuation of a continuum source.

Applications to Petroleum. In some cases, FAA has been used directly for analyzing petroleum samples (*13, 14, 15, 16*). These analyses, in which the sample is diluted in a suitable combustible solvent and aspirated into the flame, are generally applied at concentrations above 1 ppm. Although the use of organic solvents increases FAA sensitivity for most metals, the technique was not well suited for the Project target level of 10 ng/g. This was because the dilution ratios required to eliminate matrix effects caused by such factors as viscosity and volatility were so large that FAA no longer had sufficient sensitivity.

Indirect FAA methods, in which the hydrocarbon matrix is eliminated and the analyte is concentrated, could have been applied to all elements studied by the Project if a large enough sample were used. However, since indirect techniques still may encounter chemical (interelement) interferences, a minimum of 5 ml of solution must be available so that standard additions techniques can be applied. Some trace metals have been determined in petroleum by indirect FAA after a 100-g sample had been ashed (*17*). However, ashing such large samples, particularly crudes or residual fractions, is difficult and time consuming. Sulfated ash procedures were used in the Project to prepare various petroleum matrices for determining Cd, Co, Mo, Ni, and V by FAA. However, procedures were developed only for the first three elements, and cross-check data were collected only for cadmium. Since alternate techniques had greater sensitivity and allowed smaller samples to be ashed, flame atomic absorption was not widely used.

In Analysis of Petroleum for Trace Metals; Hofstader, R., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1976.

Heated Vaporization Atomic Absorption

Heated vaporization atomic absorption (HVAA) has been described extensively. HVAA differs from conventional atomic absorption in that an electrically heated device replaces the flame. The characteristics of HVAA are microliter sample consumption, sensitivity down to picogram quantities, and applicability to a wide variety of solutions. These characteristics have led to its widespread use. In petroleum analyses, this technique has been used to determine relatively high levels (ppm) of lead in gasoline, metals in used oils, and nickel and vanadium in crude oils (*18*). The Trace Metals Project has extended application of this technique to the determination of Be, Cd, Co, Cr, Mn, Mo, Sb, and V at the 10-ng/g level.

Instrumentation. Most commercially available HVAA systems consist of three components: a programmable power transformer, a "sheathing gas" control, and a workhead which holds the atomizer in the optics of the spectrophotometer. An aliquot of a sample is injected into the atomizer, which is continuously sheathed with an inert gas; then a multistep heating cycle is initiated at the power transformer. In the heating cycle, the sample is sequentially dried, ashed (pyrolyzed), and atomized at temperatures as high as 3000°C (Figure 3.2). The temperature in

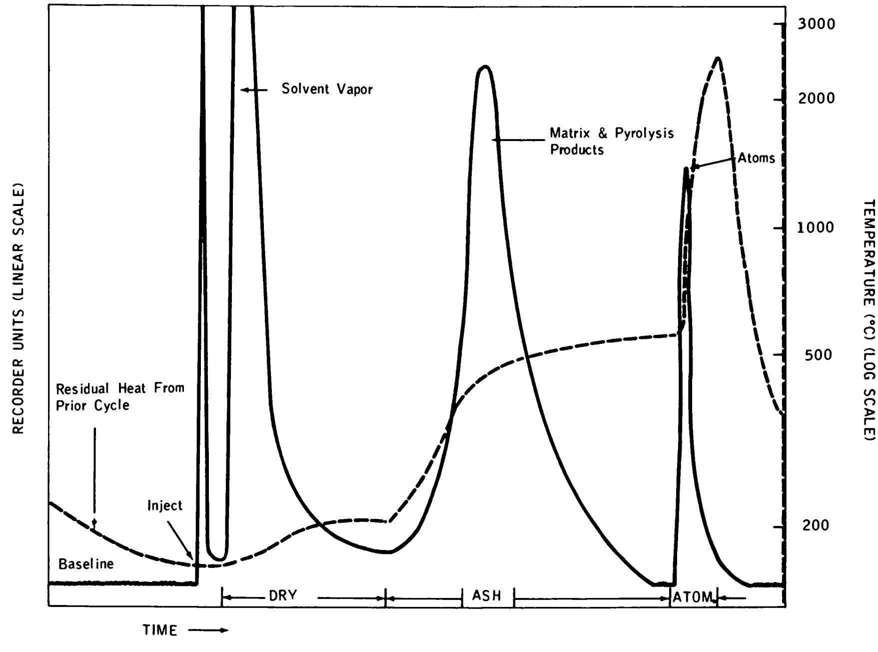

Figure 3.2. Processes in HVAA heat cycle

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each cycle may be varied by programming a voltage setting and a heating duration. For most practical applications, the background-corrected absorption peak height during the atomization is used for quantitative purposes.

Although there are several atomizer designs (*19*), the "tube furnace," in which the atoms are surrounded by the heating element, generally suffers fewer interferences. Two instruments based on this design were used by the Project to develop procedures: the Varian-Techtron carbon rod atomizer, model 63 (Figure 3.3), and the Perkin-Elmer heated graphite atomizer HGA-70 equipped with a grooved style furnace (Figure 3.4). Several other HVAA systems are commercially available and are probably satisfactory; however, their application to petroleum was not evaluated. Specific details of the components and operation of the HGA-70 and CRA-63 have been described (*20, 21*). The basic differences between these instruments may be summarized as follows:

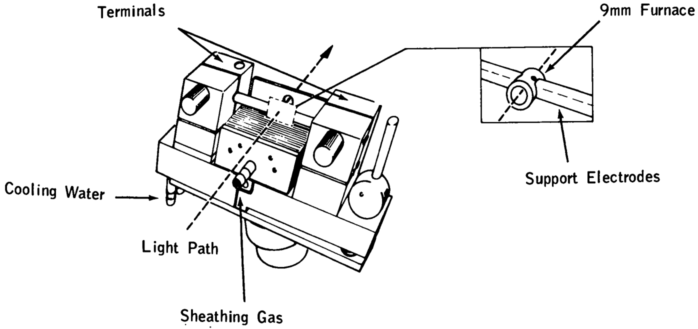

Figure 3.3 Varian-Techtron model 63 carbon rod atomizer

- The HGA-70 uses a 10–100-μl sample; the CRA uses a 1–5-μl sample
- The sheathing gas sweeps through the HGA-70 furnace whereas it passes around the CRA-63 tube.
- The optical beam passes through the "cone" type electrical contacts in the HGA-70 workhead; the support electrodes are not in the optics in the CRA-63 workhead.
- The HGA-70 with the grooved style furnace attains a maximum temperature of 1950°C; the CRA-63 reaches nearly 3000°C.

For most elements, the two systems have comparable sensitivity. Their physical differences, however, require that different procedures be developed for application to petroleum. Before such procedures can be developed, the influence of the operating parameters and the sample matrix must be considered for each element. This frequently requires considerable effort.

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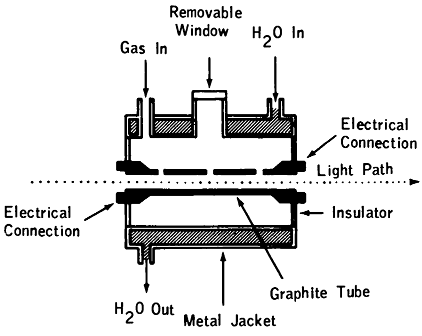
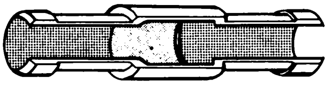
Atomization. The atomization temperature and the rate at which it is attained influence the kinetics and thermodynamics of the atomization (*22, 23*). In practice the input power is set sufficiently above the temperature required for atomization to give sharp narrow peaks while maintaining linearity over a reasonable concentration range. The temperature to be used is determined experimentally by varying the input voltage on the power transformer. To obtain comparable operation between the Project laboratories, the atomization conditions were specified in terms of a temperature–voltage correlation for the HGA-70 (*24*) and by measurement of the voltage and amperage dissipated across the CRA-63 workhead (*25*). More modern instruments are provided with electrical feedback systems to allow temperature monitoring (*26*), and even more elaborate systems have been used for theoretical studies (*27*).



A. HGA - 70 WORKHEAD



B. GROOVED STYLE TUBE

Cross-section of the grooved graphite tube.

Figure 3.4. Perkin-Elmer heated graphite atomizer

Over the atomization temperature range (~ 1200°–3000°C), carbide formation between many metal oxides and graphite is favored thermodynamically (*28*). While carbide formation has been used to explain poor sensitivity for elements such as boron or tungsten, which form refractory carbides, little attention was initially devoted to the interference caused by carbide formation with other elements. However,

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during the Trace Metals Project, reduced sensitivity was encountered with Al, Be, Cr, and Mn when the grooved furnace HGA-70 combination (maximum temperature 1950°C) was used (*24*). In studies carried out by the Project, carbide formation was shown to play a part in the atomization processes for these elements. The detection limits can be improved by pretreating the furnace with microgram quantities of such elements as lanthanum or zirconium which are thermally stable at that temperature. This technique is discussed in Chapter 6. Several alternate techniques have been reported to minimize or eliminate carbide formation, including foil furnace liners (*29*), refractory metal furnaces (*30*), and high temperature grooved-type furnaces (*31*). Although these approaches may prove useful in the future, none of them was evaluated by the Project.

Ashing. Because various reactions occur in the 300°–1200°C range, ashing conditions may affect the atomization signal. Salts such as sulfates, nitrates, and acetates may be converted to oxides. Other compounds may be reduced by the graphite to free metal which may be lost by volatilization before atomization, or they may form carbides which are more difficult to atomize. Losses of analytes by molecular distillation have been reported for aqueous samples where volatile inorganic salts may be formed (*32*). Volatile organic compounds, such as tetramethyllead, can be lost by a similar mechanism (*33*). Studies have shown that losses of the analyte can be controlled in some cases by adding reagents that form thermally stable compounds (*34*).

Sheathing Gas. The sheathing gas, which protects the furnace from oxidation during atomization, sometimes influences the response. The flow pattern, composition, and flow rate of the inert gas all affect the residence time of the atoms in the optics. In the CRA-63 the gas flows past the furnace, and gaseous diffusion is the controlling factor. In the HGA-70 the atoms are continuously swept out the ends of the furnace so that the gas velocity may influence response. For most HVAA analyses, argon or nitrogen is used as the sheathing gas; however, nitrogen has been reported to give smaller background absorption with some complex matrices (*35*). With the CRA-63, hydrogen can be added to the sheathing gas to obtain a hydrogen diffusion flame which further protects the furnace from oxidation (*20*). This addition of hydrogen can also be advantageous for atomizing some refractory elements but could lead to pre-atomization losses (*25*). In the Project the effect of hydrogen addition was studied for Be, Cr, and Mn. Hydrogen added to argon did give increased response for Cr, but when it was added to nitrogen, the response was suppressed for all three elements. Thorough studies have shown a complex relationship between hydrogen concentration, diluent inert gas, and total sheathing-gas flow rate (*36*). The procedures developed by the Project use either nitrogen or argon alone, since they were found

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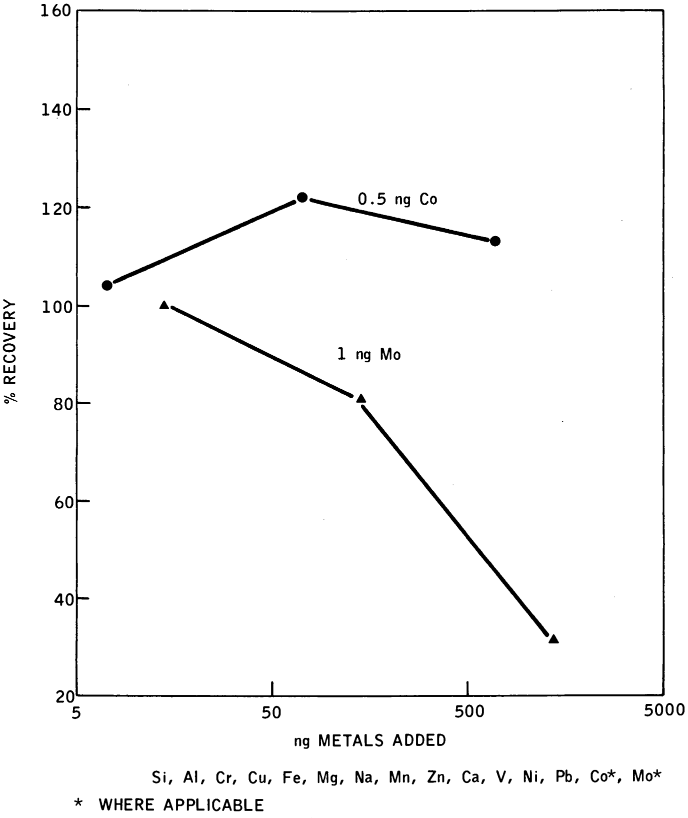

Figure 3.5. Interference in the determination of Co and Mo by HVAA (aqueous solution)

to be adequate. With the HGA-70, flow to the furnace is set at 1 l/min. With the CRA-63 the flow rate is varied from 4 to 7.5 l/min, depending on the element.

Matrix Effects. Physical wetting of graphite by petroleum samples allows these matrices to spread on the furnace surface and gives rise to a difference in response for different matrices. The HGA-70 grooved furnace has a unique axial heat profile (*22*) which minimizes spreading of organics. Spreading in CRA-63 is minimized by injecting samples while the atomizer is warm. Improved precision was attained by injecting samples and standards at fixed time intervals. Since both furnaces have an axial heat profile which results in decreased atomization efficiency away from the central injection point, calibration standards should be prepared in the same solvent as the samples to be measured.

The presence of other elements in the sample matrix may also con-

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tribute to differences in response. Both enhancement and suppression were encountered in studies conducted by the Trace Metals Project. For example, as discussed in the individual element chapters, the effect of 14 elements all present simultaneously was studied at 10, 100, and 1000-fold excesses of each for Co and Mo (Figure 3.5) and for Ni and V (Figure 3.6). Since Fe, Ni, and V are the predominant metals present in crude oils, their possible interference was specifically investigated in the HVAA analyses for Be, Cr, Mn, and Sb. The only interference by these elements which was clearly identified was a suppression of the Cr response by V. Because petroleum matrices vary so widely, a comprehensive study of interelement interferences was impractical. Since the linearity of the response was independent of the interfering metals, the procedures developed by the Project used the method of standard additions to compensate for possible interelement effects.

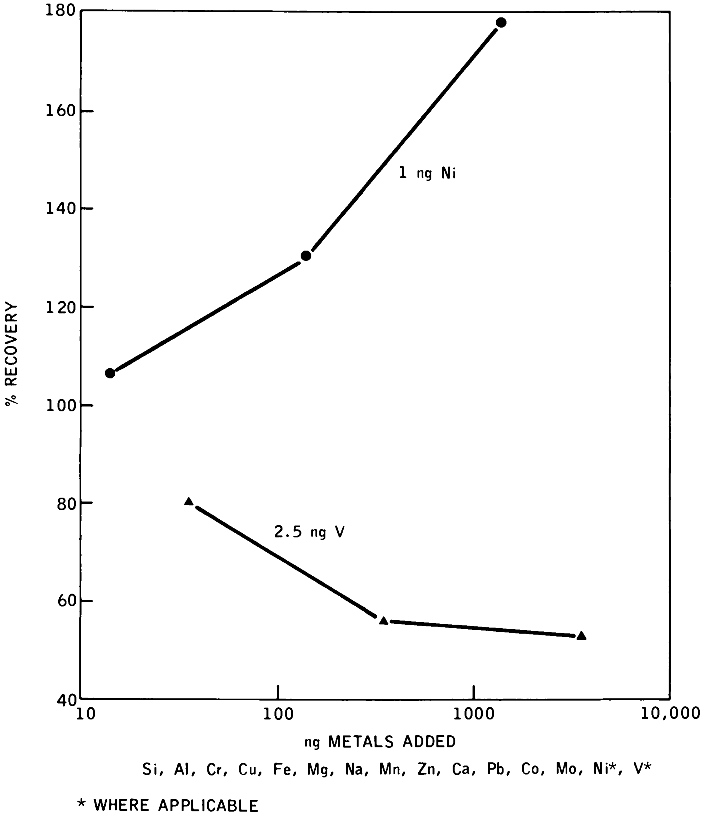

Figure 3.6. Interference in the determination of Ni and V by HVAA (aqueous solution)

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Table 3.II. Determination of Nickel in Petroleum

	Direct HVAA		*Indirect HVAA*	
Sample	*Calib. Curve, ppm*	*Std. Additions*	*Sulfated Ash Std. Additions*	*Other*
Residual Fuel (NBS; GM-5)	102	—	—	93 ± 1.2 (certified)
#6 Fuel Oil (EPA/NBS round robin)	39	—	—	39 (round robin)
Asphalt	95	—	—	100 (emission spec)
Crude A	28, 22	—	—	29.2 (neutron activation)
Crude B	0.33	0.34	0.60, 0.65, 0.65	0.7 (emission spec.)
Crude C	0.97	0.51	1.3, 1.2, 1.1, 2.0	1.7 (emission spec.)
Crude D	0.31	0.15	1.9, 1.9, 2.1	1.8 (emission spec.)
Crude E	5.5	5.3	8.5, 8.6, 8.5	10 (emission spec.)

Direct Analysis vs. Analysis after Matrix Destruction. Many HVAA analyses may be carried out directly in diluted petroleum matrices. However, difficulties arise in HVAA analyses where readily atomized elements such as Cd, Hg, Pb, or Sb are to be measured in heavy petroleum matrices which contain a significant high boiling fraction. Under conditions suitable for complete matrix removal, the elements are volatilized before atomization; if conditions are selected to prevent losses in the ashing cycle, the residual organic matrix leads to an unacceptable background absorption. For example, no suitable conditions were found by the Project for the direct HVAA determination of Cd or Pb in matrices heavier than No. 2 heating oil. This problem is not restricted to volatile elements, however, since molecular losses can also arise. For example, the low nickel results obtained by direct HVAA analyses of some crude oils (Table 3.II) are attributed to molecular distillation of volatile porphyrin compounds (*37*). In the Trace Metals Project a separate procedure involving matrix destruction of some type was used to check complete recovery for each direct HVAA procedure.

External sample decomposition procedures, such as ashing or acid digestion, not only eliminate the matrix but also convert the analyte to some specific salt suitable for HVAA analyses. For example, the ashing used to obtain data in Table 3.II converted the nickel to its sulfate. In the Project, indirect HVAA procedures were successfully applied to six elements. The application of these procedures, however, may be restricted by contamination or by reagent blanks. For example, exposure to nichrome heating elements affects chromium (*see* p. 19). Although destruction techniques eliminate the hydrocarbon matrix, they do not compensate for interelement interferences.

Electroanalytical

A resurgence of interest in electroanalytical techniques during the past several years has been described by Flato (*38*) as a "Renaissance." For some time, developments of other techniques, particularly atomic absorption spectroscopy, coupled with the non-availability of commercial instrumentation, had caused a deterioration of interest in the practical applications of electroanalysis. However, rapid advances in electronic technology have now resulted in the commercial availability of sophisticated, versatile, reliable, yet relatively inexpensive electroanalytical instrumentation which is easy to operate.

Although modern electroanalytical techniques are characterized by high sensitivity (sub-nanogram levels are measurable), a degree of selectivity, a capability for multi-element analysis, and excellent accuracy and precision, these techniques have not been widely applied for trace elemental analysis in the petroleum industry, primarily for two reasons:

(1) the basic incompatibility of the petroleum matrix with the inorganic solution requirements of the most commonly applied electrode systems

(2) the sensitivity and applicability of atomic absorption spectroscopy.

Nevertheless, modern methods of electroanalytical chemistry can, in certain instances, either successfully complement atomic absorption spectroscopy or provide information not otherwise obtainable. A synergistic effect can, in fact, be obtained by a combination of the two techniques, and such work has been described by Lund and Larsen (*39*) and by Fairless and Bard (*40*). Controlled potential electrolysis is first used to preconcentrate the element or elements of interest on an electrode. This step also separates the elements from the matrix and possibly from interfering elements. The electroplated elements are then removed and measured by atomic absorption. The combination of the two techniques seems ideal for problems in petroleum trace metal analysis. Much research remains to be done, however, before its applicability can be defined.

Applicable Techniques. Several electroanalytical techniques that use commercially available instrumentation (*41, 42*) are applicable to trace elemental analysis:

(1) Linear sweep voltammetry
(2) Differential pulse polarography
(3) AC polarography
(4) Linear sweep anodic stripping voltammetry
(5) Differential pulse anodic stripping voltammetry

Of these, anodic stripping voltammetry (*43*), both linear sweep and differential pulse, incorporates a pre-concentration feature and therefore provides a capability for determining sub-nanogram levels of some elements that is limited only by the degree to which contamination can be controlled. In addition to being extremely sensitive, anodic stripping voltammetry is highly selective. It is applicable to approximately 20 elements which form electroreversible amalgams. With proper choice of the electrolyte system, multi-element analyses are possible. Precision, accuracy, and linearity of response are excellent, and quantitation can be accomplished either by standard additions or by use of an internal standard (*44*).

Application of Electroanalysis to Petroleum Products. Because petroleum matrices are incompatible with the usual inorganic solution requirements, extensive sample preparation is required before the sample can be transformed into a form amenable to electroanalysis. Since acids such as sulfuric, nitric, fuming nitric, perchloric, or various mixtures of them are used in decomposing petroleum matrices, treatment to remove or neutralize the residual strong acid is required before the analysis can proceed. This often involves the addition of various reagents, resulting in high reagent-to-sample ratios. Consequently, extremely high-purity reagents must be used. Unfortunately, few ultrahigh-purity reagents are commercially available, and even these may not be satisfactory for some analyses. The element to be determined will dictate the choice of both sample digestion scheme and type of final analyte solution. A critical consideration is the amount of contamination introduced during the entire process. Reagent purity problems are not, however, entirely restrictive because it is sometimes possible to prepare high purity reagents by relatively simple techniques in the analytical laboratory just before analysis.

Considering these limitations, a procedure for lead determination has been developed as a result of the Project and is described fully in Chapter 10. Preliminary work related to cadmium determination suggests that a similar technique can be used to determine other elements and can be expanded to a multi-element capability for trace metals in petroleum.

Optical Emission Spectroscopy

The most important feature of optical emission spectroscopy in addition to its usefulness in measuring trace amounts, is its ability to measure a number of metals simultaneously. Although the technique is not sensitive enough to measure nanogram/gram concentrations by direct analysis, the metals can be concentrated by ashing the sample. With most petroleum samples, ashing can easily provide a concentration factor of several thousand. However, in ashing, highly volatile elements such as arsenic, mercury, and selenium may be lost. The instrumentation is expensive

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but, if available, permits a good semiquantitative measurement for nanogram/gram levels of many metals in petroleum and a more or less permanent record.

As part of the Trace Metals Project, a procedure was developed in which 100 g of oil is ashed with sulfuric acid and sufficient high purity magnesium nitrate to yield 50 mg of ash. The magnesium nitrate is converted to magnesium sulfate and acts as a carrier for the trace metals. The resulting ash is mixed with pelletizing graphite and pressed into an electrode. This electrode is sparked using a graphite counter electrode, and the resultant spectrum is recorded on a photographic plate. The spectral intensities are then compared with the intensities of standards that have been carried through the entire procedure.

Data obtained on a jet fuel spiked with 20 and 100 ng of metal per gram appear in Table 3.III. At the 100-ng/g level, the recovery is within 25% of the amount added. Similar data obtained on crude oil indicate recovery of approximately ±50%. Some elements which may be present in high concentration in the ash, such as nickel and vanadium, cause difficulty in interpretation of the spectrum. Nevertheless, this technique is useful as a screening procedure to identify the presence or absence of certain elements at trace levels before more extensive analysis.

Table 3.III. Analysis of "Spiked" Jet Fuel for Trace Metals by Emission Spectroscopy

	Found, ng/g									
Added, ng/g	*Be*	*Cd*	*Co*	*Cr*	*Mn*	*Mo*	*Ni*	*Pb*	*Sb*	*V*
20	6	9	11	9	19	13	14	17	17	11
100	85	75	123	85	113	108	128	113	115	113

Neutron Activation

The availability of high flux thermal neutron irradiation facilities and high resolution intrinsic Ge and lithium drifted germanium (Ge(Li)) or silicon (Si(Li)) detectors has made neutron activation a very attractive tool for determining trace elemental composition of petroleum and petroleum products. This analytical technique is generally referred to as instrumental neutron activation analysis (INAA) to distinguish it from neutron activation followed by radiochemical separations. INAA can be used as a multi-elemental method with high sensitivity for many trace elements (Table 3.IV), and it has been applied to various petroleum materials in recent years (*45–55*). In some instances as many as 30 trace elements have been identified and measured in crude oils by this technique (*56, 57*).

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Even with the availability of high resolution solid state detectors, it is sometimes desirable or even necessary to resort to post-irradiation chemical separations to eliminate interfering isotopes and to improve sensitivity and accuracy (*58, 59, 60*). These radiochemical manipulations may include any of the conventional chemical separations, such as precipitation, solvent extraction, ion exchange, volatilization, chromatography, or electrodeposition. A brief discussion of this topic has been prepared by Ross (*61*).

Table 3.IV. Activation Analysis Detection Limits[a]

Element	*Detection Limit ng/g*
Aluminum	5
Antimony[b]	5
Arsenic[b]	5
Barium	50
Bromine	1
Cadmium	100
Chlorine	100
Chromium	100
Cobalt[b]	10
Copper	10
Dysprosium	0.1
Gallium	5
Gold	1
Indium	0.1
Lanthanum	10
Manganese[b]	1
Mercury[b]	5
Molybdenum[b]	100
Nickel	100
Potassium	100
Rhenium	1
Selenium[b]	10
Silver	5
Sodium	10
Tellurium	100
Titanium	100
Tungsten	5
Vanadium	10
Zinc	100

[a] Data based on 1-hr irradiation at 10^{12} n cm^{2-} sec^{-1} and optimum counting conditions.

[b] Elements determined by neutron activation by the Trace Metals Project.

Trace metal studies of petroleum have also been made using the Cockroft-Walton neutron generator, a positive ion accelerator, producing either 2.4 or 14.5 MeV neutrons which can be thermalized. The thermal

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neutron flux, however, is several orders of magnitude less than is produced by a nuclear reactor, and therefore only a few elements may be detected in the parts-per-million range (*62*, *63*).

To evaluate the applicability of instrumental neutron activation analysis, the Trace Metals Project used the services of a commercial reactor activation facility and performed the gamma counting and data processing at one of the participating laboratories. This technique was used to measure seven of the 13 elements investigated as part of the Project's analytical methods cross-check program and to study sample storage stability. The seven elements were: antimony, arsenic, cobalt, manganese, mercury, molybdenum, and selenium. The elements not studied were excluded because their small cross-sections or short half-lives were unfavorable for measurements at the desired 10-ng/g level. The significant nuclear properties of the seven elements studied are shown in Table 3.V. Note that the half-lives of the isotopes are long enough to have allowed transfer from the reactor to the laboratory located about 45 miles away. The calculated activity indicates the relative analytical sensitivity of each element and aided in selecting optimum irradiation and counting conditions.

Table 3.V. Elements Determined by INAA and Their Nuclear Properties

Element	*Isotope*	*Half-Life*	*Prominent Gamma Rays (KeV)*	*Calculated Activity (d/m/μg at T_0)*
Antimony	^{122}Sb	64.3 hr	564	1300
Arsenic	^{76}As	26.4 hr	559	3700
Cobalt	^{60}Co	5.3 yr	1170 1333	9
Manganese	^{56}Mn	2.6 hr	847	10^5
Mercury	^{197}Hg	65.0 hr	77.6	125
Molybdenum	^{99}Mo	66.7 hr	141	23
Selenium	^{75}Se	120 days	136	1.5

The irradiation was performed in a 250-kw water pool reactor operating at a steady state flux of 10^{12}n cm^{-2} sec^{-1}. The irradiation times ranged from one hour for As, Hg, Mn, Mo, and Sb to three or more hours for Co and Se. Sample and standards were prepared and sealed in ultrapure quartz vials. During irradiation the vertical reactor neutron flux profile was monitored by including aqueous cobalt solutions spaced at regular intervals. After irradiation for the specified time, the samples were returned to the laboratory for counting and data processing. The counting equipment consisted of an ORTEC lithium-drifted germanium detector coupled to a Nuclear Data 1024 channel analyzer.

To meet ERDA (formerly AEC) license requirements, the activity of each sample received was monitored with a radiation survey meter, and the personnel involved were supplied with radiation dosimeters. An excellent discussion of radiation safety and licensing requirements in handling reactor-activated petroleum products is available (*49*).

Sample Encapsulation. The popular polyethylene snap-cap, heat-sealed vials, used in the initial phases of the work, were found to be unsatisfactory because of post-irradiation losses of mercury and had to be replaced by quartz vials. Since ^{197}Hg has a convenient half-life, initially no special attempts were made to count the samples immediately after arrival from the reactor facilities, and they were processed whenever time and sample scheduling permitted. The first set of data, obtained five days after irradiation, indicated that the petroleum stocks spiked with mercury had lost 50–60% of their ^{197}Hg activity when compared with aqueous standards; the latter showed only the expected decrease in activity caused by decay. A second set of the same samples was irradiated and counted the same day; in this case the mercury recovery was more nearly quantitative. Repeated experiments showed that if the samples were irradiated in polyethylene and counted within four to eight hours, excellent recoveries of mercury were obtained (Table 3.VI). Subsequent experiments confirmed that organomercury compounds can be reduced to elemental mercury in hydrocarbon matrix during irradiation and the mercury is then lost by diffusion as vapor (*64*). Even with prompt counting, however, the use of quartz vials offers advantages.

Table 3.VI. Post-Irradiation Loss of Mercury from Polyethylene Sample Vials (ng/g Hg Measured)[a]

Counted 4-8 hr after Irradiation	*Counted 24-28 hr after Irradiation*	*Counted 120-124 hr after Irradiation*
103	101	49
98	94	46
97	91	40
96	90	38
97	97	48

[a] Standard solution was prepared to contain 100 ng/g of mercury.

Storage Stability Studies Using INAA. During the Trace Metals Project, INAA was chosen to monitor the stability of petroleum stocks spiked with organometallic mercury and arsenic compounds and stored in five containers including glass, Vycor brand, and plastic. This study was done to find the best container for storing and shipping samples to members of the Project as part of the program to cross-check new chem-

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ical methods submitted for validation. The results of this study appear in Tables 2.III and 2.IV.

Use of INAA in Trace Metals Project Validation Studies. As, Co, Hg, Mn, Mo, Sb, and Se in petroleum were determined by INAA as part of the Project's analytical methods cross-check program. Except for selenium all elements were determined by a 1-hr irradiation followed by gamma-ray spectroscopy. Counting times ranged from 10 min to one hour. As and Sb were determined simultaneously with a high resolution germanium detector capable of separating the 559-KeV gamma-ray of ^{76}As and the 564-KeV ^{122}Sb gamma. Mn is one of the elements "tailor made" for analysis by neutron activation because of the large cross-section and 100% abundance of ^{55}Mn. However, a fairly rapid transfer from the reactor to the counting facilities was necessary because of the 2.6-hr half-life of ^{56}Mn.

Because of the long half-life of ^{75}Se, selenium was determined by irradiating the samples intermittently over one to two weeks while other irradiations were in progress at the reactor facilities. Following irradiation the samples were counted for up to 15 hr to reach the 10-ng/g level.

The results of cross-checks comparing the INAA and the chemical methods developed by the Trace Metals Project are discussed in the chapters dealing with the specific elements. The chemical analysis data in most part represent the average of triplicate results from two or more laboratories, and the neutron activation results are the average of two or more irradiations and varying counting conditions. Overall results are summarized in Figure 1.2.

Use of Commercial Facilities. How can the average analytical chemist without a reactor of his own obtain good defensible analytical results by neutron activation? The following are recommended guidelines:

- Discuss the problem with reactor personnel.
- If possible, do sample preparation, counting, and data processing in house.
- Prepare samples and standards of identical geometry.
- Include neutron flux monitors.
- Specify length of irradiation.

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4

Antimony

Two reports of the presence of antimony in petroleum have appeared in the literature; both studies used instrumental neutron activation analysis (INAA) as the analytical technique. In one study antimony was found in unspecified amounts in five of the 20 crude oils which were surveyed (*1*); in the other, antimony was found in 10 crude oils in amounts ranging from 30 to 107 ng/g (*2*).

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Available Analytical Methods

Methods applicable to the determination of trace quantities of antimony in organic matrices, except for neutron activation analysis, require the matrix to be destroyed before the antimony is measured. Wet oxidations using nitric, sulfuric, and perchloric acids have been used for samples of blood and tissue (*3*), and low temperature ashing has been used for samples of filter paper and ion exchange resins (*4*).

After the organic matrix is destroyed and an aqueous solution containing the antimony is obtained, various analytical techniques can be used to measure submicrogram amounts of antimony. These techniques include conventional flame atomic absorption spectroscopy (*5, 7*), anodic stripping voltammetry (*8*), polarography (*9*), colorimetry (*10, 11, 12*), fluorimetry (*13, 14*), and optical emission spectroscopy (*15*). Recently, submicrogram amounts of Sb have been determined by stibine generation into a hydrogen–argon, entrained-air flame of an atomic absorption spectrometer (*16, 17, 18, 19*), and heated vaporization atomic absorption techniques have been applied at the nanogram level (*20*).

Role of Neutron Activation

Antimony can be readily determined in petroleum at a concentration of less than 10 ng/g by instrumental neutron activation analysis with a 1-hr irradiation at a neutron flux of 10^{12} n cm^{-2} sec^{-1}. The principle radiation arising from the ^{121}Sb (n, γ) ^{122}Sb activation and subsequent decay of ^{122}Sb occurs at 564 KeV. With a high resolution Ge(Li) detector antimony may be measured in the presence of ^{82}Br (550 KeV) and ^{76}As (559 KeV), which may be found in some petroleum matrices.

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Special Analytical Considerations

An important consideration in the determination of antimony in aqueous matrices is the fact that antimony can be present in the (III), (IV), or (V) valence state. To avoid analytical problems, it is desirable that the antimony be present in a specific valence state. This is particularly important if a spectrophotometric method is to be used because the reagents employed usually react only with a particular oxidation state. Maren observed in a study of the use of rhodamine B that Sb(IV) could not be easily oxidized to the required Sb(V) (*3*). In work on the determination of antimony using 3,4,7-trihydroxyflavone, a reagent which reacts only with Sb(III), Fider demonstrated that Sb(IV) and Sb(V) could be reduced to Sb(III) by hydroxylamine sulfate (*13*).

Sample Preparation

The method developed by the Trace Metals Project involves a decomposition step in which the matrix is destroyed, followed by treatment to ensure that antimony is present as Sb(III) before measurement by atomic absorption.

In the decomposition step, the sample is heated with sulfuric acid, and the carbonaceous residue is burned off in a muffle furnace. The resultant ash is dissolved in hydrochloric acid, treated with hydroxylamine to reduce the antimony to the trivalent state, and stabilized with tartaric acid. Other ashing aids, such as nitric and perchloric acids or magnesium nitrate, have been used with success in determining antimony (*21*), but these were not investigated for use because of the observations regarding antimony measurement by heated vaporization atomic absorption which are discussed below.

Measurement

In the proposed method antimony is measured by heated vaporization atomic absorption (HVAA), using a Varian-Techtron CRA-63 atomizer. The detection limit is 2 ng Sb/ml with solutions of Sb(III). When blank determinations were made, no signals at the 217.6-nm antimony line were obtained for 50% solutions of sulfuric acid or nitric acid. However, solutions containing a mixture of both acids did give signals at the 217.6-nm Sb line. The response was linear with the amount of nitric acid in the sulfuric acid solutions. Similar phenomena are encountered when hydrogen peroxide or hydrochloric acid were added to sulfuric acid. These findings were not investigated further, but obviously mixtures of acids must be avoided in the determination of antimony by HVAA.

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The effect of iron, nickel, and vanadium on the signals obtained from antimony solutions in 50% sulfuric acid was investigated. Antimony signals from solutions containing 15 ng Sb/ml and 28.2 μg/ml each of iron, nickel, and vanadium were suppressed by 14% compared with those obtained when no metals were added. Consequently, the method of standard additions was adopted to compensate for interferences of this type.

Recommended Method

Antimony as triphenylstibine was added to two crude oils and a No. 2 heating oil in amounts ranging from 14 to 273 ng/g. The spiked oils along with their unspiked counterparts were analyzed using the proposed method. The results are presented in Table 4.I. Based on 23 replicate analyses at a concentration of 65 ng/g or less, the standard deviation was 8.6 ng/g.

Table 4.I. Recovery of Antimony by Proposed Method[a]

	Antimony Concentration (ng/g)	
Oil	*Added (as Triphenylstibine)*	*Measured*
Crude oil A[b]	65	61
Crude oil B	14	13
Crude oil B	54	44
No. 2 heating oil	27	25
No. 2 heating oil	273	268

[a] Unspiked oils contained < 10 ng Sb/g.
[b] Crude oil A contains 76 μg V/g and 21 μg Ni/g.

A crude oil, a No. 2 heating oil, and a naphtha were selected for an interlaboratory evaluation of the procedure. Since these oils were found to contain less than 10 ng Sb/g, triphenylstibine was added to each of the oils so that the samples contained 46.2 ng Sb/g. The antimony content was then determined by the proposed method and by instrumental neutron activation analysis. The average antimony content, as determined by the initiating laboratory, the cooperating laboratory, and by neutron activation is given in Table 4.II. The average antimony value for the three spiked samples was 46.7 ± 4.6 ng/g as determined by the initiating laboratory, 43.4 ± 4.5 ng/g as determined by the cooperating laboratory and 53.3 ng/g as determined by neutron activation. The pooled data from the two laboratories using the recommended method gave a value of 45.3 ± 4.7 ng/g.

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Table 4.II. Interlaboratory Analysis for Antimony by the Proposed Method and by Neutron Activation

Sample	*Antimony Concentration (ng/g)* HVAA *Initiating Laboratory*	HVAA *Cooperating Laboratory*	*INAA*
No. 2 heating oil			
unspiked oil	< 10	< 10	13
46.2 ng Sb/g added	47	39	66
Naphtha			
unspiked oil	< 10	< 10	< 10
46.2 ng Sb/g added	48	48	60
South Louisiana crude			
unspiked oil	< 10	< 10	< 10
46.2 ng Sb/g added	45	43	47

Detailed Procedure

Scope. This method can be used to determine 10–250 ng of Sb/g in petroleum or petroleum products. Larger amounts may be determined by using smaller samples.

Summary of the Method. The sample is digested with concentrated sulfuric acid until most of the sulfuric acid is removed and a carbonaceous residue remains. The sample is then placed in a muffle furnace to destroy the carbonaceous material. Hydrochloric acid and hydroxylamine hydrochloride are added to dissolve the inorganic residue and reduce antimony(V) and antimony(IV) to antimony(III). Tartaric acid is then added to complex antimony(III), and the solution is evaporated to a small volume. The antimony content of this solution is determined by heated vaporization atomic absorption using the method of standard additions.

Apparatus

(1) *Heated vaporization atomizer.* Varian Techtron carbon rod atomizer model 63 (CRA-63) or equivalent.

(2) *Atomic absorption (AA) spectrophotometer,* with 0.5-sec response time, equipped with an antimony hollow cathode lamp.

(3) *Recorder,* with millivolt range(s) compatible with the AA spectrometer and with a similar 0.5-sec response time. A Jarrell-Ash model 82-500 AA spectrometer and a Leeds and Northrup Speedomax W 10 mV recorder were used in the development of this method.

(4) *Syringe,* with Teflon tip or Teflon needle, capable of reproducibly delivering 5-μl aliquots.

(5) *Micropipets,* 20- and 100-μl (capillaries, syringe or Eppendorff type devices are suitable).

(6) *Vycor crucibles,* 50 ml.

(7) *Hot plate,* continuously variable to 500°C.

(8) *Muffle furnace,* capable of operation at 550°C.

Reagents. Unless otherwise stated, reagents are ACS reagent grade. Water is deionized or distilled.

(1) *Sulfuric acid,* concentrated.

(2) *Hydrochloric acid,* 6*N* dilute concentrated hydrochloric acid 1:1 with water.

(3) *Hydrochloric acid,* 1*N* dilute concentrated hydrochloric acid 1:12 with water.

(4) *Hydroxylamine hydrochloride solution,* 10% w/v in water.

(5) *Tartaric acid solution,* 10% w/v in water.

(6) *Standards*

(a) 1000 μg/ml antimony stock solution, Fischer Scientific Co. (SO-A-450), or equivalent.

(b) 5 μg/ml antimony solution, prepared fresh daily by dilution of the 1000 μg/ml antimony stock solution with 1*N* hydrochloric acid.

(c) 50, 100 and 150 ng/ml antimony solutions, prepared fresh daily. 100, 200, or 300 μl of the 5 μg/ml antimony solution, 0.5 ml of the hydroxylamine hydrochloride solution, and 1 ml of the tartaric acid solution made up to 10 ml with 1:1 hydrochloric acid.

Instrument Operation

(1) Place the CRA-63 tube furnace in the optical beam of the AA spectrophotometer and optimize the alignment. The analytical wavelength is 217.6 nm.

(2) Optimize the CRA-63 operating parameters and AA spectrophotometer by using 5 μl of the 50 ng/ml antimony solution to obtain a signal of approximately 25% of scale. Use the following settings as a guide in optimizing the instrument.

Sample size	5 μl
Inert gas	N_2-7.5 l/min. @ 10 psi (setting 10 on rotometer)
CRA-63 program	
dry	3/20 sec
ash	7.75/30 sec
atomize	8.5/2 sec

The performance of the carbon tube may be monitored by atomizing an aliquot of a 50 ng/ml Sb "control solution" during the analyses. The absorption for control solution should remain within 20% of its original signal during an entire run.

(3) Determine that the absorbance for antimony is linear with concentration to 150 ng/ml by injecting 5 μl of 50, 100 and 150 ng/ml antimony solutions. If the absorbance is not linear with concentration for these solutions, more dilute antimony solutions must be prepared to establish the linear range of the instrument. This linear range must not be exceeded during the *Measurement* part of the procedure.

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Procedure

Carry a reagent blank through the procedure.

(1) *Ashing*

(a) Weigh approximately 2.0 g of the sample into the Vycor crucible.

(b) Add 5 ml of concentrated sulfuric acid to the sample, swirl the mixture and allow to stand for 5 min. Place the crucible on a hot plate, decompose the sample, slowly at first with low heat from the hot plate, and increase the hot plate setting gradually until fumes of sulfuric acid appear.

(c) When fumes of sulfuric acid have almost ceased, transfer the beaker to a muffle furnace at 550°C and ash the residue for 1 hr.

(d) Cool the crucible. If carbonaceous matter remains, add three to four drops of concentrated sulfuric acid, heat the crucible on the hot plate until most of the sulfuric acid is removed, and return the crucible to the muffle furnace for 0.5 hr.

(e) Repeat Step (d) until only the light color caused by inorganic matter remains.

(f) Add 15 ml of 1:1 hydrochloric acid and three drops (*ca.* 0.15 ml) of the hydroxylamine hydrochloride solution, place a watch glass on top of the crucible and boil gently for 15 min.

(g) Remove the watch glass, add five drops (*ca.* 0.25 ml) of the tartaric acid solution, and reduce the volume in the crucible to approximately 2 ml by evaporation.

(h) Transfer the contents of the crucible quantitatively into a 10-ml beaker with 1:1 hydrochloric acid.

(i) Reduce the volume of liquid in the beaker to approximately 2 ml. Since the volume does not enter into the calculation, an exact volume measurement is not required.

(2) *Measurement*

(a) With the Teflon-tipped syringe, pipet 5 μl of the solution into the tube furnace of the CRA-63, initiate the heating cycle, and record the peak height attributable to antimony absorption during the atomization cycle.

(b) Repeat Step (a) four more times.

(c) Calculate the average peak height, omitting any peaks which result from obvious injection errors, and record it as A_0.

(d) Add 20 μl of the 5 μg/ml antimony standard (100 ng) to the beaker, mix well, and repeat Steps (a) and (b).

(e) Calculate the average peak height and record it as A_1.

(f) Repeat Step (d).

(g) Calculate the average peak height and record it as A_2.

Calculation

(1) Calculate the total antimony for the sample and reagents as follows:

$$\text{ng Sb} = \frac{1}{2}\left[\frac{(100\text{ ng Sb})\ (A_0)}{A_1 - A_0} + \frac{(200\text{ ng Sb})\ (A_0)}{A_2 - A_0}\right]$$

(2) Calculate the antimony content of the reagents in the same manner.

(3) Calculate the antimony content of the sample:

$$\frac{\text{ng Sb}}{\text{g sample}} = \frac{\text{ng Sb (sample + reagents)} - \text{ng Sb reagents}}{\text{2 g sample}}$$

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Arsenic

As a result of the recent concern with environmental contamination, the need to quantitatively measure trace concentrations of arsenic in petroleum and related materials has taken on new and important emphasis. The concentration of arsenic in crudes can approach the low part-per-million level, but more typically it is in the nanogram/gram (part-per-billion) range. Although several sophisticated methods are applicable at the part-per-billion level, a need has existed for a method that could be carried out in a typical petroleum laboratory.

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Available Analytical Methods

Gravimetric methods and chemical methods, such as colorimetric measurements based on the arsenic–molybdenum blue complex (*1, 2, 3*) and arsine generation in combination with silver diethyldithiocarbamate (*4, 5, 6, 7*), have been used to measure arsenic in aqueous media. Various instrumental methods such as differential pulse polarography (*8*), heated vaporization atomic absorption (*9*), arsine generation in combination with atomic absorption spectroscopy (*10, 11, 12*) or non-dispersive atomic fluorescence spectroscopy (*13*), and optical emission spectroscopy (*14*) can be used to determine arsenic in aqueous solutions.

Of the readily available measurement techniques, atomic absorption in combination with arsine generation has gained great popularity and widespread use in recent years. This popularity is primarily the result of the ease of applicability and high sensitivity of the technique. However, prior to the studies carried out in the Trace Metals Project, no systematic study of its application to petroleum matrices had been made.

Role of Neutron Activation

Arsenic levels below 10 ng/g can be readily detected in petroleum by instrumental neutron activation analysis. The most convenient technique involves direct gamma counting based on the ^{75}As (n, γ) ^{76}As reaction with a principle radiation of 559 keV. After a 1-hr irradiation at a neutron flux of 10^{12} n cm^{-2} sec^{-1}, the arsenic may be counted in a relatively short time. The method requires a high resolution Ge(Li) detector to avoid interference from bromine (550 keV) or antimony (564 keV).

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Special Analytical Considerations

Because of its volatile nature, arsenic is one of the more difficult elements to retain quantitatively during the matrix destruction phase of the sample preparation. The determination is further complicated by the fact that arsenic can occur in inorganic and/or organic forms, and the analytical method must be capable of determining both forms. Since the classical measurement techniques are applicable only to inorganic forms of arsenic, the organic arsenic in the petroleum must be converted to the inorganic form before the measurement step. During destruction of the organic matrix the arsenic must be kept in the As(V) oxidation state by maintaining strong oxidizing conditions. Under weak oxidizing or reducing conditions As(V) may be converted to As(III), which is volatile and is easily lost.

There are several potential interferences in the determination of arsenic by hydride generation at the nanogram/gram level. Large reagent blanks can seriously complicate the determination; however, most commercial acids are relatively free of significant quantities of arsenic. Although arsenic is one of the few elements which can be converted readily to a volatile hydride, other hydride-forming elements such as antimony and selenium can interfere. In addition, some materials can change the rate of hydride generation and thus influence the results. Considering these decomposition and measurement interferences, the Project studied each portion of the procedure separately.

Sample Preparation

Since the measurement technique is applicable only to aqueous solutions, the determination of arsenic in organic matrices such as petroleum requires that the matrix be destroyed prior to the arsenic measurement. The form in which arsenic occurs in petroleum is not known. However, the volatile nature of arsenic contributes to the low recovery by techniques such as dry ashing. Dry oxidation using magnesium oxide and magnesium nitrate as ashing aids (*2, 6, 10*), and wet oxidation involving various combinations of sulfuric, nitric, perchloric, and periodic acids (*1, 3, 15*), have been used to destroy the organic matrix of plants, animal tissue, and coal.

During the Trace Metals Project, dry ashing with ashing aids such as .sulfur or magnesium oxide gave low recovery, probably because of loss of arsenic by volatilization. Quantitative recovery from spiked samples was obtained by Wickbold combustion techniques under highly optimized conditions. However, it was extremely difficult to maintain optimized conditions throughout the entire sample preparation scheme. Raney nickel scavenging techniques gave 100% recovery of both organic

Table 5.I. Recovery of Arsenic by Proposed Method

Matrix	*Arsenic Form*	*Arsenic Concentration (ng/g)* *Added*	 *Measured*
Mineral oil	Sodium Arsenite ($NaAs_2O_4 \cdot 7H_2O$)	10	9.8
	”	30	29
	”	50	46
	Triphenylarsine	10	9.2
	”	30	33
	”	30	34
	”	50	54
No. 2 heating oil	”	50	53
Crude No. 1	”	30	37
Crude No. 2	”	99.4	96

and inorganic arsenic from clean systems such as distilled water and xylene. However, low results were obtained in more complicated systems such as crude oils. Subsequent studies demonstrated that the low recovery was caused by incomplete adsorption of arsenic by the Raney nickel. A similar study using silica gel as the scavenger gave erratic results.

A wet oxidation procedure which utilizes sulfuric, nitric, and perchloric acid was established as a satisfactory method for destroying the organic matrix of petroleum samples with quantitative retention of the arsenic. Table 5.I compares the amount of arsenic added to three petroleum samples with the amount of arsenic found on analysis by the method subsequently adopted. In each case the amount found by analysis agrees with the amount added within the precision of the method and indicates that the arsenic is quantitatively retained by the sample preparation procedure. Quantitative retention of the arsenic was further substantiated by neutron activation analysis of a sample which was spiked with a known amount of triphenylarsine. The arsenic concentration was determined at each step of the sample preparation procedure (Table 5., II). The results were in general agreement with the amount added and confirmed the earlier conclusion that arsenic is quantitatively retained during sample preparation.

Measurement

Several measurement techniques were evaluated in conjunction with arsine generation. Some colorimetric techniques have adequate sensitivity but are subject to numerous interferences. The precision of the Gutzeit technique was inadequate to meet the requirements of the Project. An atomic absorption technique, based on a commercial arsine generation

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Table 5.II. Confirmation of Quantitative Arsenic Recovery by Neutron Activation

	Arsenic Concentration (ng/g)	
Sample Treatment	*Added (Corrected for Volume Changes)*	*Measured by Neutron Activation*
None (spiked No. 2 fuel oil)	493	495
After addition of $HClO_4$	90	75
After addition of H_2SO_4 and HCl	26	29
After addition of KI and $SnCl_2$	21	22

apparatus that collects gases in a balloon, gave inconsistent results because of changes in the elasticity of the balloon. In an alternate approach, arsine was collected in a liquid nitrogen cold trap, and the arsenic was subsequently measured by atomic absorption. The technique gave adequate sensitivity and precision, but the analysis required a prohibitive amount of time per sample. Arsine generation in conjunction with a hydrogen–argon entrained air flame was established to be the most satisfactory means of measuring arsenic at the 0.1-μg level.

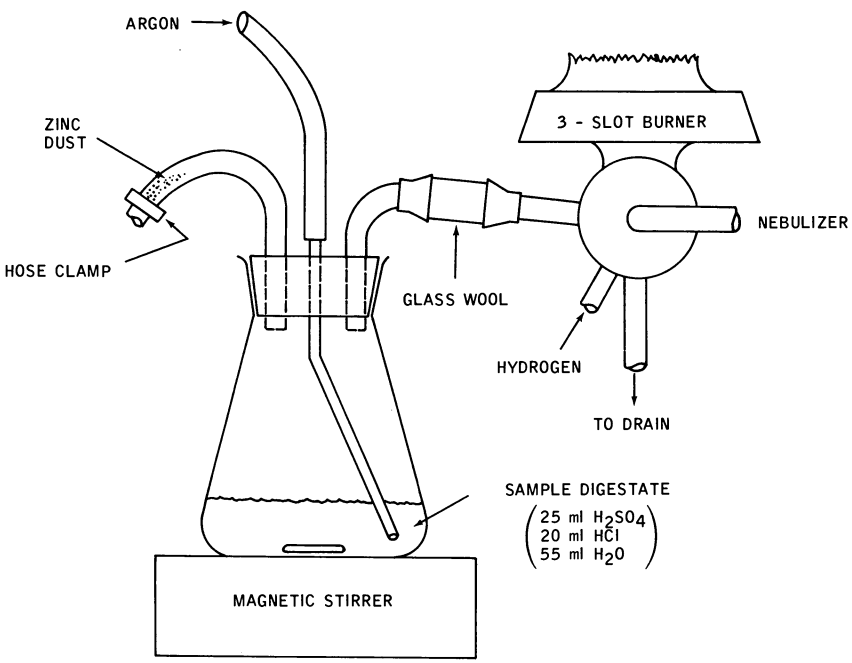

Figure 5.1. Arsine-generating apparatus

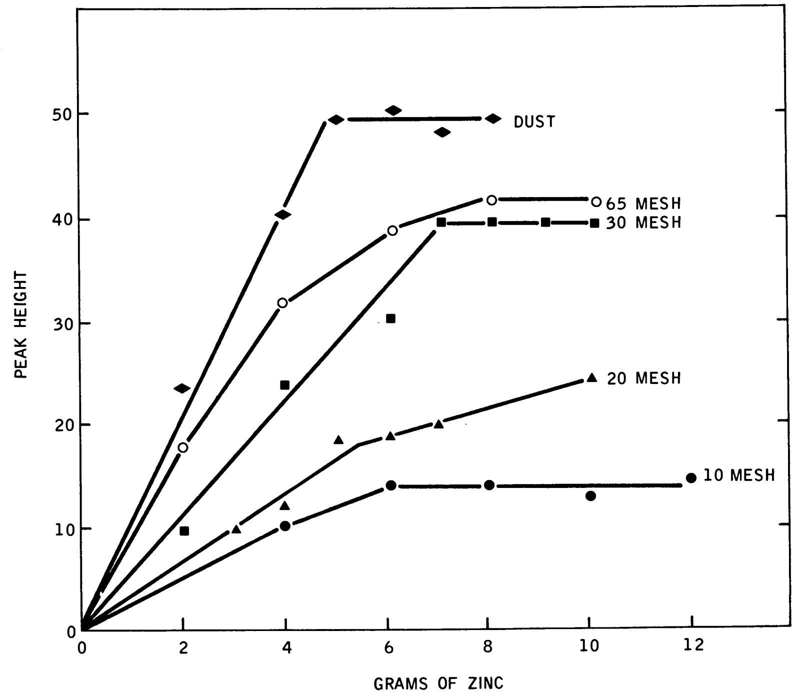

Figure 5.2. Arsenic response vs. grams of zinc

Potassium iodide, sodium borohydride, titanium trichloride and zinc dust were evaluated as reducing agents to convert the arsenic to arsine. The results with the sodium borohydride and titanium trichloride were more erratic than those obtained with potassium iodide and tin(II) chloride. Optimum generating conditions using the apparatus shown in Figure 5.1 were established empirically. The effect of zinc particle size and total amount of zinc added is shown in Figure 5.2. Seven grams of zinc dust gave the largest, most reproducible response and was used for all subsequent measurements. The effect of acid concentration on arsenic response is shown in Figure 5.3. Maximum sensitivity is obtained with a generating solution composed of 25 ml of sulfuric acid, 20 ml of hydrochloric acid, and 55 ml of water.

The generation of arsine is affected by other ions in the generating solution. Although nitrate ions depress the arsenic signal (Figure 5.4), copper, potassium, ammonium, and sodium have no apparent effect. Concentrations of selenium greater than 100 ng reduce the peak *height* response but up to 50 μg do not affect the peak *area* response (Figure 5.5). This indicates that selenium affects the rate of generation but not the quantity generated. Since the selenium concentration of most petroleum

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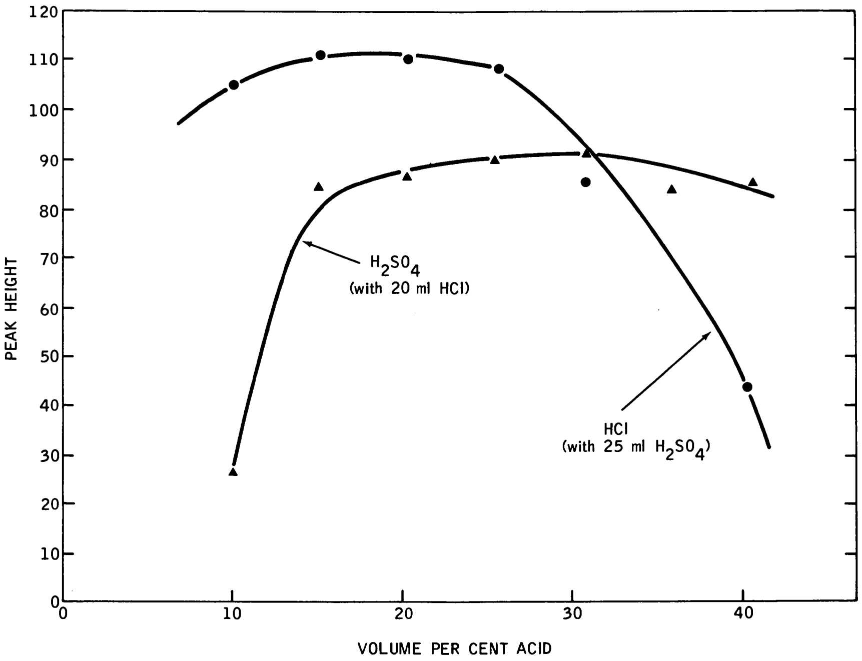

Figure 5.3. Arsenic response vs. acid composition

products is quite low, no adverse effect by selenium on arsenic measurement by this measurement technique is expected.

The optimum instrument parameters for arsenic measurement were established with a Perkin-Elmer model 403 atomic absorption spectrometer. Better sensitivity was obtained at the 197.2 nm arsenic line than at the 193.7 nm line. Some investigators have recommended the use of a quartz or silicon furnace for arsenic measurement (*16, 17, 18*). However, the hydrogen–argon entrained air flame in combination with the described arsine generation apparatus offers comparable sensitivity. A hollow cathode lamp was used throughout the development of the method. Subsequent studies have shown that a five-fold improvement in sensitivity can be obtained with an electrodeless discharge lamp.

Recommended Method

A 10-gram sample is wet digested with sulfuric, nitric, and perchloric acids in a beaker. The sample digestate is transferred to an arsine-generating flask, and KI and $SnCl_2$ are added to convert the arsenic to As(III). The flask is connected to the AA instrument, and zinc dust is added. The spike signal is corrected by subtracting the appropriate blank signal, and the arsenic concentration is determined by relating the

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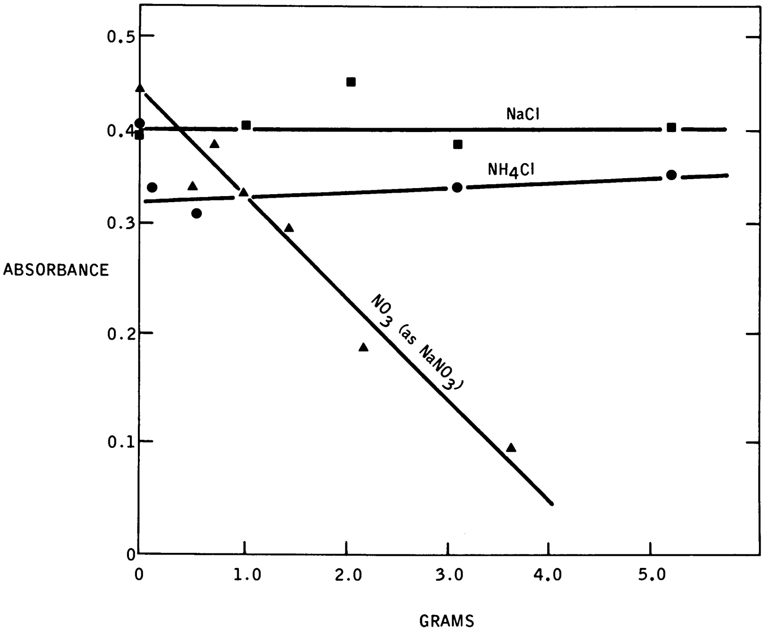

Figure 5.4. Effect of other salts on arsenic response

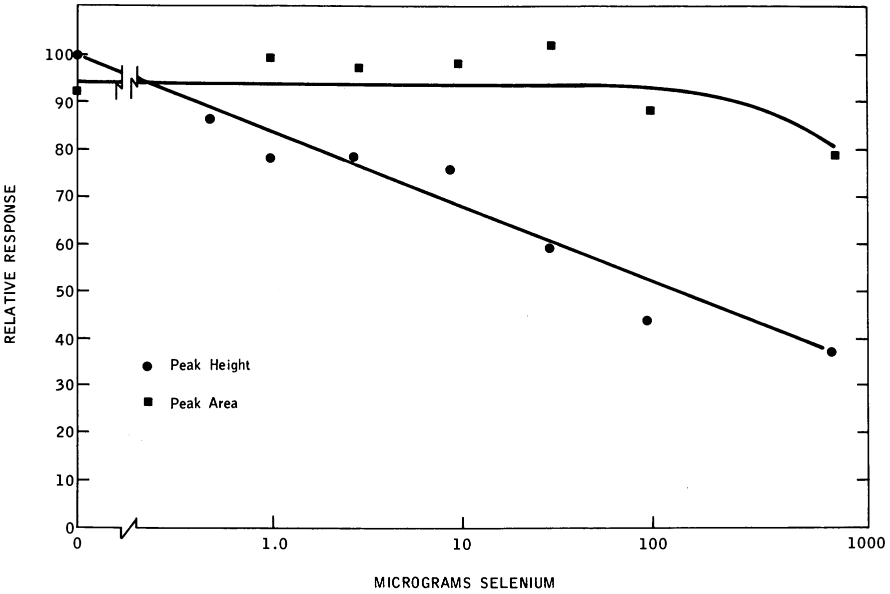

Figure 5.5. Effect of selenium on arsenic response

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corrected signal to a standard calibration curve prepared from aqueous arsenic standards.

The precision of the method was established by repetitive analysis of crudes that contained native arsenic and crudes to which known amounts of arsenic, as triphenylarsine, had been added. Both peak height and peak area measurements were made. The results are presented in Table 5.III. The relative standard deviation over the 10–100 ng As/g concentration range is 22% for the peak height measurement and 32% for the peak area measurements. Since better precision was obtained by peak height measurements, it is recommended that this measurement be used in preference to peak area measurement unless selenium is present.

Table 5.III. Precision of Proposed Arsenic Method

	Measurement			
	Peak Height		*Peak Area*	
	$\overline{X}$ *ng As/g*	*RSD* *%*	$\overline{X}$ *ng As/g*	*RSD* *%*
Crude A	55.7	20.3	44.6	18.4
Crude B	9.6	39.6	12.6	62.7
Crude B +30 ng As/g	37.2	14.8	41.8	21.3
Crude B +99.4 ng As/g	95.6	12.3	75.4	25.5

The accuracy of the method was evaluated by analyzing petroleum samples to which known amounts of arsenic had been added. In each case the amount found by analysis agreed with the known spike level within the precision of the method.

The method was evaluated in three cooperating laboratories. Two petroleum samples that contained native arsenic were analyzed as blind samples by the initiating laboratory and by the two cooperating laboratories. A third sample was spiked with triphenylarsine and analyzed by the initiating laboratory and by the two cooperating laboratories. The initiating laboratory knew the spike level, but the two cooperating laboratories analyzed the samples as blind samples. Each sample was also analyzed in a fourth laboratory by neutron activation. The results are presented in Table 5.IV. The results obtained in the different laboratories by the arsine generation–atomic absorption method on the samples that contained native arsenic agree within the precision of the method. The results obtained on the spiked sample also agree with the known spike level within the precision of the method. In addition, the results obtained by the arsine generation–atomic absorption method compare favorably with the results obtained by neutron activation, supporting the validity of both techniques.

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Detailed Procedure

Considerable experience with this procedure is necessary before reliable analyses can be obtained. It is recommended that an oil sample of known arsenic concentration be analyzed repeatedly until the necessary skills are developed to obtain correct results before analyzing samples of unknown concentration.

Scope. This method is used to determine 10 to 100 ng/g (10 to 100 ppb) of arsenic in petroleum and petroleum products. Higher concentrations can be determined by reducing the sample size. Sample preparation requires about 8 hr. However, the preparation time per sample can be reduced to about 1 hr by preparing sample in batches of eight to ten. At one point in the procedure the sample is allowed to digest overnight. Consequently, sample preparation must be started one day and completed the next.

Table 5.IV. Interlaboratory Analysis for Arsenic by the Proposed Method and by Neutron Activation

	Arsenic Concentration (ng/g)			
	Initiating Laboratory	*Cooperating Laboratories*		*Neutron Activation*
		A	*B*	
Crude	65.0	56	62	53
Diesel fuel	21.5	18	21	18
No. 2 heating oil	< 10	< 10	< 10	2
No. 2 heating oil + 50 ng As/g	49.0	53	42	53

Summary of Method. The organic material from 10 g of sample is oxidized with sulfuric, nitric, and perchloric acid. The sample digestate is transferred to an arsine-generating flask, and the acid concentration is adjusted for optimum generation of arsine. The As(V) is reduced to As(III) with potassium iodide and tin(II) chloride, and the arsenic is converted to arsine by the addition of zinc dust. The arsine is carried into the hydrogen–argon entrained air flame of the atomic absorption instrument by a stream of argon. The spike type signal is corrected by subtracting the appropriate blank signal, and the arsenic concentration is determined by relating the corrected signal to a standard calibration curve prepared from aqueous arsenic standards.

Instrumentation

(1) *Atomic absorption instrumentation.* Perkin-Elmer model 403 or equivalent instrument, equipped with deuterium background corrector, arsenic hollow cathode lamp, triple-slot burner head and a strip chart recorder.

(2) *Arsine generation apparatus.* (*see* Figure 5.1).

(a) Preparation of zinc doser. Bore a 15-, 10- and 8-mm hole in the rubber stopper. Insert a 10-cm by 1.1-cm id Tygon tube through the 15-mm hole. Clamp the free end with a hose clamp. Insert a bent 8-mm glass tube through the 8-mm hole and connect the top end to the argon supply with a 0.6-cm id Tygon tube. Insert a 20.3-cm by 0.6-cm id Tygon tube through the 10-mm hole and attach the other end to the drying tube. Fill the drying tube loosely with glass wool and connect the drying tube to the oxidant inlet of the burner with a 0.6-cm id Tygon tube.

(b) 500-ml Erylenmeyer flask

(c) Plastic drying tube. 5-cm long, filled loosely with glass wool.

(d) Magnetic stirrer. Variable speed.

(3) *Gases* (*cylinders*). Argon and hydrogen, equipped with two-stage regulating valves.

(4) *Pyrex beakers.* 600- and 100-ml, one for each sample and blank. (The 100-ml beaker must have volume graduation marks for each 25 ml.)

(5) *Watch glasses.* Appropriate to cover 600 and 100-ml beakers.

(6) *Broken glass tube boiling chips.*

(7) *Hot plate.* Variable heat control.

(8) *Funnel.* 40-mm powder funnel.

(9) *Thermometer.* 0° to 500°C temperature range.

Reagents. All reagents are ACS reagent grade unless otherwise noted. All references to water indicate distilled water.

(1) *Sulfuric acid,* concentrated.

(2) *Nitric acid,* suitable for mercury determination (J. T. Baker, or equivalent).

(3) *Perchloric acid.* 70-72%, suitable for mercury determination (J. T. Baker, or equivalent).

(4) *Hydrochloric acid.* Concentrated (DuPont, or equivalent).

(a) Dilute hydrochloric acid. Dilute 267 ml of concentrated hydrochloric acid to 1.0 l with water.

(5) *Potassium iodide.* (Mallinckrodt, or equivalent).

(a) 20% Potassium iodide solution. Dissolve 20 g of potassium iodide in water and dilute to 100 ml with water.

(6) *Tin(II) chloride dihydrate.* (Mallinckrodt, or equivalent).

(a) 20% Tin(II) chloride solution. Dissolve 20 g of stannous chloride dihydrate in 50 ml of concentrated hydrochloric acid and dilute to 100 ml with water.

(7) *Zinc.* Metallic dust (Mallinckrodt, or equivalent).

(8) *Arsenic standards*

(a) Reference standard. 1000 μg/ml, Fisher Scientific HSO-A-449 or any arsenic standard certified for atomic absorption analyses.

(b) 1.0 μg/ml Arsenic standard. Dilute 0.10 ml of the 1000 μg/g arsenic reference standard to 100 ml with water. This solution should be prepared daily to avoid possible concentration changes during storage.

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Sample Preparation. All samples should be analyzed in duplicate, and the preparation should be carried out in a well-ventilated hood.

(1) Weigh 10 g of sample into a 600-ml beaker. Two blanks should be prepared with each batch of samples.

(2) Add a broken glass boiling chip, 25 ml of concentrated sulfuric acid and 10 ml of concentrated nitric acid. Insert a 500°C thermometer and cover the beaker with a watch glass. Place on a room temperature hot plate and slowly increase the temperature until fumes of nitrogen dioxide appear. Maintain the temperature at about 200°C and add 5-ml increments of concentrated nitric acid with sufficient frequency to produce nitrogen dioxide fumes at a steady rate.

(3) Continue adding nitric acid increments until the solution becomes homogeneous and dark brown in color. Approximately 70 ml of nitric acid will have been added, and the volume of solution in the beaker should be about 50 ml.

(4) Increase the temperature until fumes of sulfuric acid appear and continue fuming while adding concentrated nitric acid dropwise until the solution is a pale straw color. (A total of approximately 100 ml of concentrated nitric acid will have been added). Cool and transfer the material on the watch glass into the beaker with 50 ml of wash water. Heat again to the fumes of sulfuric acid. If the solution has appreciable color, repeat Step 4 using 30 ml of water.

(5) Cool, cautiously add 100 ml of water, and heat to fumes of sulfuric acid; cool and repeat with another 100 ml of water.

(6) Cool and transfer, with water, to a 100-ml beaker that has approximate volume graduation marks. Add a broken glass boiling chip and heat to fumes of sulfuric acid.

(7) Cool and add sufficient sulfuric acid to bring the total volume to the 25-ml graduation mark on the beaker. Add 2 ml of perchloric acid and cover with a watch glass. Place the beaker on a hot plate, in a hood and behind a safety shield. Close the hood door and heat at 150°C for 1 hr. If the temperature exceeds 200°C, the perchloric acid will be lost by distillation of the perchloric acid–water azeotrope.

(8) Cool to room temperature and let set overnight.

(9) Quantitatively transfer the sample digestate to a 500-ml Erlenmeyer flask with 75 ml of dilute hydrochloric acid (total volume is approximately 100 ml).

(10) Measure the arsenic response as described under Measurement of Arsenic below.

Preparation of Calibration Standards

(1) Add to each of seven 500-ml Erlenmeyer flasks 25 ml of concentrated sulfuric acid and 75 ml of dilute hydrochloric acid. Cool to room temperature, and to the flask add 0.0 (blank), 0.1, 0.2, 0.3, 0.5, 0.7, and 1.0 ml of the 1.0 ppm arsenic standard reference solution.

(2) Add to each flask 1.0 ml of 20% potassium iodide solution and 1.0 ml of the 20% stannous chloride solution.

(3) Measure the arsenic response of each solution as described below.

Measurement of Arsenic

(1) Optimize the atomic absorption instrument for maximum arsenic response. The following optimum parameters found for the Perkin–Elmer model 403 instrument serve as a guide.

Wavelength	197.2 nm
Slit	4
Burner height	17 mm
Hydrogen flow	40 on fuel control gage
Argon flow	40 on oxidant flow gage
Noise suppression	2
Scale expansion	2X, (2 mv full scale recorder response)
Chart speed	120 mm/min
Hollow cathode current	per manufacturer's recommendations
Background corrector	on

Aspirate water through nebulizer continuously

(2) Place the rubber stopper equipped with the zinc dosing tube and the argon supply hose into an empty 500-ml Erlenmeyer flask (*see* Figure 5.1), and ignite the hydrogen–argon entrained air flame. Adjust the baseline and zero the instrument.

(3) Remove the rubber stopper from the Erlenmeyer flask, invert, insert a 40-mm fluted funnel into the zinc dosing tube, and add 7 g (± 0.1) of zinc dust. It is recommended that the zinc dust be preweighed into individual containers and the entire contents of one container added to the zinc dosing tube).

(4) Place a 500-ml Erlenmeyer flask containing a sample digestate or standard on the magnetic stirrer and insert the rubber stopper. (Keep the zinc dosing tube bent so that the zinc dust does not fall into the solution). Start the magnetic stirrer and set at a fast stirring rate. (The same rate should be used for each sample and standard).

(5) Start the recorder and record the baseline. Raise the zinc dosing tube to a vertical position and quantitatively transfer the zinc dust to the solution. Record the arsenic signal until the recorder returns to the baseline. Either peak height or peak area may be used to indicate arsenic response.

(6) Remove the rubber stopper from the Erlenmeyer flask and proceed to the next sample or standard.

Calculation

(1) Obtain the net standard arsenic response by subtracting the blank arsenic response from each of the standards. Plot the net arsenic response vs. nanograms of arsenic, drawing the best line through the series of points.

(2) Subtract the sample blank response from each sample to obtain the net sample arsenic response. Relate the net response to the calibration curve to obtain the nanograms of arsenic in the sample. Divide by the sample weight to obtain the concentration, in nanograms/gram, of arsenic in the sample.

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6

Beryllium

The Environmental Protection Agency has set strict emission standards for stationary combustion sources. No more than 0.01 μg Be/m^3 may occur in the ambient atmosphere around such sources, and a maximum of 10 g may be emitted in a 24-hr period (*1*). The earth's crust is estimated to contain about 0.001% beryllium, mostly as inorganic minerals. Beryllium has been reported at the parts-per-million level in coal, and in survey analyses with emission spectroscopic techniques Russian authors have reported the detection of unspecified levels in petroleum (*2, 3, 4*).

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Available Analytical Methods

Prior to this study, no specific method for determining beryllium in petroleum has been reported. However, there exist a variety of sensitive measurement techniques that could be applied after the petroleum matrix has been mineralized. Classical colorimetric methods provide sensitivities of 0.05–0.2 μg Be although the method is not entirely specific for beryllium (*5*). The Morin fluorimetric method has good accuracy above about 0.02 μg Be, with a detection limit that may be two orders of magnitude lower (*6, 7*). Several masking steps are required to apply the procedure to complex matrices. Optical emission spectrographic techniques have a detection limit of 0.0005 μg (*8*); however, the apparent enhancement of the 234.9-nm line by iron in the sample must be eliminated. Unlike many other metals, beryllium cannot be determined by neutron activation (small neutron capture cross section), x-ray fluorescence (low mass absorption coefficient), or direct polarography (high reduction potential).

Selective, sensitive techniques based on gas chromatography or atomic absorption have been developed. The trifluoroacetylacetonate derivative of beryllium may be extracted from aqueous solutions into benzene and the beryllium determined by gas chromatography (*9*). Under optimum conditions 4×10^{-13} g can be detected with an electron capture detector (*10*). With a mass spectroscopic detector the detectible quantity is 2.5×10^{-11} g, but the specificity of the method is greatly improved (*11*). Flame atomic absorption has been used to determine beryllium in many materials (*12*). The technique can be used to measure levels down to 0.02 μg Be/ml in aqueous solutions. However, some interferences may be encountered even with the nitrous oxide–acetylene

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flame. Aluminum and silicon suppress the response, but the interference can be overcome by adding 8-hydroxyquinoline. Enhancement effects produced by other metals may be leveled by addition of excess potassium ion (*13*). A detection limit of about 10^{-12} g may be obtained by HVAA techniques. Large excesses of calcium may suppress the signal, but the effect can be circumvented by the addition of 1% sulfuric acid (*14*). The HVAA technique offers the unique advantage that it may be applied directly to the petroleum sample without prior mineralization.

Special Analytical Considerations

Most analytical procedures for beryllium in organic matrices require mineralization before measurement. Both ashing and digestion procedures have been used. In the Trace Metals Project the total blank for 125 ml of nitric acid and 25 ml of sulfuric acid heated to dryness was less than 5 ng of Be. When this combination of acids was used to decompose spiked petroleum samples, only 80% recoveries were obtained. These low recoveries are attributed to incomplete solubilization of the salts formed when the digestate was heated to dryness. Low recoveries have also been reported in the wet oxidation of orchard leaves with nitric and sulfuric acids in an open beaker (*15*). Although this was originally attributed to losses of volatile beryllium compounds, subsequent work suggests that the apparent loss is an artifact of the gas chromatographic procedure that had been originally used (*16*). In the same work, it was noted that many environmental samples have been successfully analyzed for beryllium after either wet oxidation or dry ashing. Even beryllium acetylacetonate or its more volatile fluorinated derivatives may be mineralized without loss of beryllium if proper solubilization techniques are used (*17, 18*).

Sample Preparation

In the procedure developed by the Project the only sample preparation required is dilution of the sample with an appropriate solvent such as tetrahydrofuran. Since sample preparation is kept to a minimum, the opportunity for contamination is reduced, and losses from sample handling are minimal.

Measurement

During the Trace Metals Project two procedures based on measurement by HVAA were developed for determining beryllium in petroleum matrices (*20*). One procedure utilizes the CRA-63 carbon rod atomizer,

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and the other uses the HGA-70 graphite furnace atomizer. Each procedure is discussed below.

CRA-63 Procedure. The optimum operating parameters for the determination of beryllium with the CRA-63 carbon rod atomizer as established by this study are presented in the detailed procedure at the end of this chapter. The effect of operating parameters (ashing power, inert gas flow rate, etc.) on the instrumental response of beryllium has been reported (*20*).

Even under optimal conditions there is considerable variation in the magnitude of the signal from the same amounts of beryllium in different matrices (Figure 6.1). The peak height response for a specific amount of beryllium as the organic sulfonate in tetrahydrofuran is about one-half that obtained from the same amount of beryllium in dilute sulfuric acid. The response in crudes averages about the same as that in the solvent alone but varies from one crude to the next. In acid digests of the crudes, the response increases to about the same level as that obtained in aqueous sulfuric acid, but the variation between different crudes is still evident. This suggests that the beryllium response is affected by some inorganic species that occurs naturally in petroleum. An exhaustive search for the interfering species was not undertaken, but it was established that the

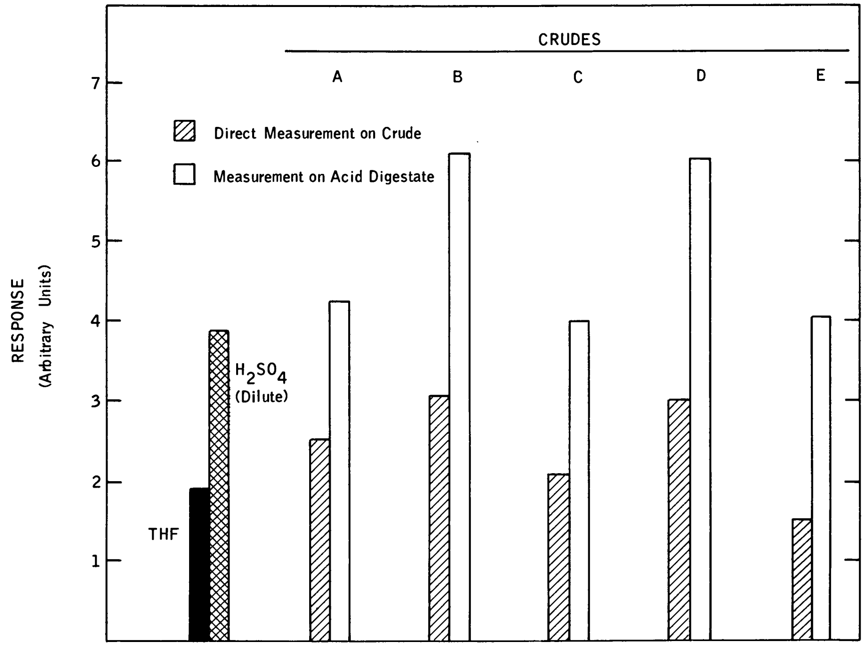

Figure 6.1. Effect of matrix on Be response (CRA-63 procedures)

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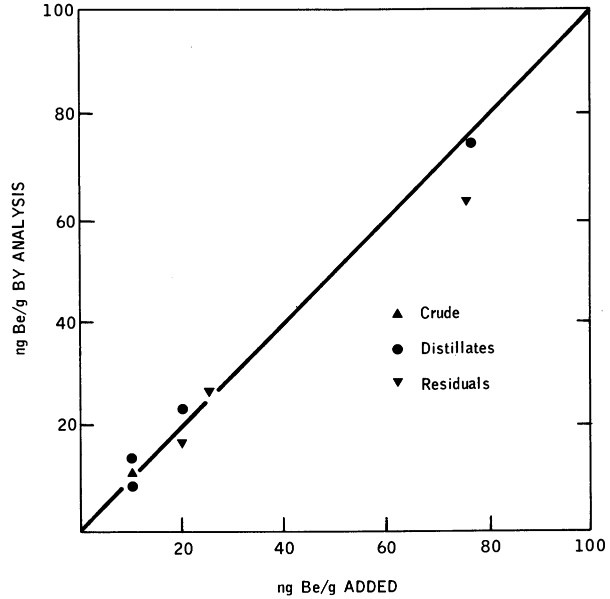

Figure 6.2. Analysis of known materials for Be (CRA-63 direct-standard addition procedure)

variation in response was not caused by iron, nickel, or vanadium—the three most prevalent metals in crudes.

The variation in response for the same amount of beryllium in different crudes prohibits the use of calibration curve techniques. Consequently, the method of standard additions was adopted to circumvent the variation in response. The applicability of the standard addition technique was evaluated by analyzing several types of petroleum samples that had been spiked with known amounts of beryllium using the Conostan beryllium standard. The results are shown in Figure 6.2. If the analyses were 100% accurate, all data points would fall on the diagonal "match line." All experimental values agree with the known spike level within the precision of the method, suggesting that the standard addition technique compensates for the variation in response.

HGA-70 Procedure. In the development of this procedure, a HGA-70 graphite furnace atomizer was used with a Perkin-Elmer 403 dual-beam spectrophotometer equipped with a deuterium background corrector. With the HGA-70 it is necessary to use grooved-type furnaces for petroleum samples to prevent the sample from running out the end of the furnace. The grooved furnaces attain a maximum temperature of 1950°C. At this temperature beryllium forms a stable carbide which prevents quantitative atomization and drastically reduces the beryllium response (*21*). Quantitative atomization can be obtained, and the beryllium signal significantly increased, by coating the inner surface of the furnace with an element such as lanthanum or zirconium that forms a thermally stable carbide when heated to elevated temperatures in the presence of carbon. Satisfactory coatings can be obtained by placing an aqueous or organic solution of the carbide-forming element into the furnace and heating the furnace through the three-stage heating cycle. These carbide coatings are stable for the normal useful life of the furnace (150-200 determinations) and are not destroyed by exposure to the atmosphere.

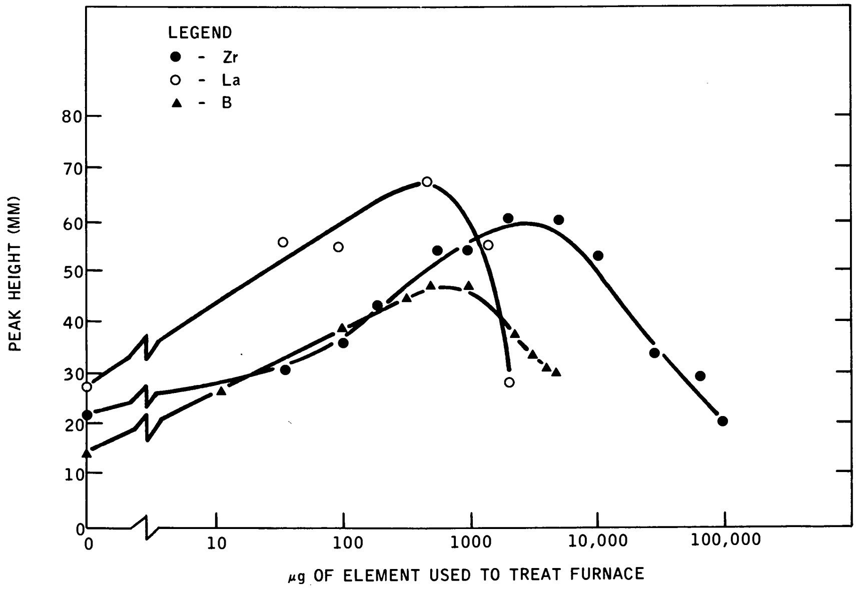

Figure 6.3. Effect of carbide coating on beryllium signal

These coating effects were studied as part of the Project (*21*). Enhancement of the beryllium peak height response passed through a maximum as the amount of carbide-forming element used to coat the furnace was increased (Figure 6.3). While the beryllium peak height response was increased significantly by coating the furnace with one element, a still greater enhancement was noted when the furnace was coated with two carbide-forming elements. However, no further enhancement was obtained if the furnace was treated with additional elements.

Energy dispersive x-ray analysis of the inner surface of furnaces that had been coated in this manner indicated that the coating element was distributed uniformly over the inner surface; this suggests that the coating is formed by a reaction between the vaporized element and the graphite

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walls of the furnace. These coatings, therefore, avoid beryllium carbide formation by preventing physical contact between the sample and the graphite of the furnace.

Recommended Methods

Two methods were developed independently, in separate laboratories. The sample preparation for the two methods is essentially the same. However, because of the differences in instrumentation, separate detailed methods are required. In both methods the sample is diluted with tetrahydrofuran, and an aliquot is injected into the atomizer. The average signals for the sample and the sample plus three standard additions are obtained. After appropriate blank corrections have been made, the beryllium concentration is obtained by graphical or calculation techniques.

CRA-63 Method. The in-house precision and accuracy of the CRA-63 method were established by analysis of petroleum samples to which known amounts of beryllium (as the sulfonate) had been added. The results are shown in Table 6.I. The standard deviation over the 30–40 ng Be/g range is 3.8 ng Be/g, and the "t" test indicates that the results found by analysis agree with the amount added within the precision of the method.

Table 6.I. Recovery of Beryllium by Proposed CRA-63 Method[a]

	Beryllium Concentration (ng/g)	
Sample Matrix	*Added*	*Measured*
Crude A	12	11
	22	26
Crude B	10	10
	20	21
Diesel fuel	10	8
	20	20, 26
	76	63, 87
Atmospheric residue	10	8, 15
	20	17
	26	32, 28
	76	64
Heating oil	10	13

[a] All unspiked oils contained less than the detectable amount of beryllium.

Three petroleum samples spiked with 38.5 ng Be/g were analyzed (in three cooperating laboratories) by the CRA-63 method. The results are presented in Table 6.II along with the results obtained by the initiating laboratory. The average value obtained, independent of sample, is 34.7 ng Be/g, with a relative standard deviation of 18.7%. The relative standard deviation in any one laboratory is 12%, which compares favorably with the 10% obtained in the initiating laboratory. Laboratory 3 reported only average values, and the data were not used in the statistical evaluation of individual laboratories.

HGA-70 Method. The precision and accuracy of the HGA-70 procedure were established in the same manner by analyzing samples to which a known amount of beryllium had been added. Typical results are presented in Table 6.III. The results obtained by analysis agree with the known spike level within the precision of the method. The precision was established at three different concentration levels by multiple analysis of crudes to which a known amount of beryllium had been added. The relative standard deviations were 7.1, 6.9, and 10.0% at concentrations of 48.1, 9.8, and 1.4 ng Be/g, respectively.

Table 6.II. Interlaboratory Analysis for Beryllium by CRA-63 Procedure[a]

	Beryllium Concentration (ng/g)			
Sample	*Initiating Lab*	*Lab 1*	*Lab 2*	*Lab 3*
No. 2 heating oil	31	28	31	47
Crude A	35	47	30	49
Crude B	35	40	35	24

[a] All spiked samples contained 38.5 ng added beryllium per g of sample.

Three petroleum samples to which known amounts of beryllium had been added were used to cross-check the method in a cooperating laboratory. The results obtained by the cooperating laboratory and by the initiating laboratory are shown in Table 6.IV. The average of three determinations made on each sample by the cooperating laboratory agrees with the known spike level within the precision of the method on two samples but is slightly outside the precision of the method on the third sample. The values obtained by the initiating laboratory are within the precision of the method on all three samples.

The cross-check results obtained on both procedures suggest that either the CRA-63 or HGA-70 procedure will provide reliable and accurate analysis of petroleum for trace levels of beryllium and there should be no significant difficulties in establishing these methods in other laboratories.

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Table 6.III. Recovery of Beryllium by HGA-70 Method[a]

Matrix	*Beryllium Concentration (ng/g)* Added	Measured
Gasoline	50	50
No. 2 fuel oil	2	2
Crude A	10	11
Crude B	98	102
Crude C	10	23
No. 6 fuel oil	29	27

[a] All unspiked oils contained less than the detectable amount of beryllium.

CRA-63 Procedure

Scope. This method is capable of determining 10–1000 ng Be/g in petroleum and petroleum products. Each determination requires approximately 30 min.

Summary of the Method. The sample is diluted approximately 1:1 with tetrahydrofuran and analyzed directly using a standard additions technique and a Varian-Techtron model 63 carbon rod atomizer.

Apparatus

(1) *Carbon rod atomizer.* Varian-Techtron model 63 or equivalent.
  (a) 9-mm pyrolytically coated atomization tubes (Varian-Techtron).
  (b) FX-91 support electrodes (Poco Graphite).
(2) *Atomic absorption spectrophotometer (AAS).* Jarrell-Ash 82-582 or equivalent, equipped with a strip chart recorder.
  (a) Beryllium hollow cathode lamp.
  (b) Hydrogen continuum lamp.
(3) *Syringe,* with Teflon tip or Teflon needle, capable of delivering 1 μl samples reproducibly.
(4) *Micropipets,* 5 and 25 μl (capillaries, syringe or Eppendorf type).

Table 6.IV. Interlaboratory Analysis for Beryllium by HGA-70 Procedure

	Beryllium Concentration (ng/g)		
Sample	*Added*	*Cooperating Laboratory*	*Initiating Laboratory*
No. 2 fuel oil	35	37	33
No. 6 fuel oil	39	40	37
Shale oil product	32	47	37

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Reagents

(1) *Solvent*

(a) Tetrahydrofuran (HF), ACS Reagent Grade, stabilized.

(2) *Standards*

(a) Conostan Be standard. 5000 ppm (w/w) beryllium-in-oil standard (Continental Oil Co.).

(b) Stock standard (1000 μg/ml). Weigh 2.0 g of Conostan 5000 ppm (w/w) standard into a 10 ml volumetric flask and dilute to volume with THF.

(c) Calibration standard (5 μg/ml). Dilute 25 μl of the 1000 μg/ml stock standard to 5 ml with THF.

Procedure

(1) Weigh 2.5 g of oil sample into a 5-ml volumetric flask and dilute to volume with THF.

(2) Adjust the atomizer in the optics so that a minimum atomization blank is obtained when the system is operated under optimum conditions. Use the following settings as a guide in optimizing the instrument.

Spectrometer

analytical wavelength	234.9 nm (12 mA on Be hollow cathode lamp)
background	234.9 nm (13 mA on H_2 continuum lamp)
spectral band width	0.33 nm

CRA-63

inert gas	4 l/min (nitrogen)		
cooling water	4 l/min		
injection frequency	90 sec		
dry cycle	1.5 setting	0.004 kW	20 sec
ash cycle	6.5 setting	0.13 kW	30 sec
atomize cycle	8.5 setting	1.30 kW	3 sec

The optimum values may vary slightly between instruments; the values given here serve only as guidelines.

(3) Aliquot 1 μl of the sample solution into the syringe tip.

(4) Initiate the CRA-63 program and immediately inject the sample aliquot.

(5) Record the absorbance peak height during the atomization. If the absorbance is greater than 0.05, prepare a more dilute solution by secondary dilution with THF or by weighing a smaller sample.

(6) Repeat Step 5 twice.

(7) Average the response for the three injections. If the three values agree within 10%, use that average as the sample absorbance in the calculation; if not, repeat Step 5 twice more and use the average of the five injections.

(8) Record the average absorbance for the sample solution as A_0.

(9) Add 5 μl of the 5 μg Be/ml standard (25 ng Be) to the sample and mix well.

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(10) Obtain the average beryllium response for the spiked sample by injecting sample aliquots as in Steps 4-7.

(11) Record this average value as A_1.

(12) Repeat Steps 9 and 10 twice more to obtain average signals for the addition of 50 and 75 ng beryllium.

(13) Record these values as A_2 and A_3, respectively.

(14) Measure the background absorbance at 234.9 nm for the sample with the hydrogen continuum lamp.

Calculation

(1) Calculate the concentration of beryllium in the original sample using the following equation:

$$\text{ng Be/g oil} = \frac{A_o - b}{W(\text{g})} \times \frac{(25\text{ ng})(i)}{A_i - A_o}$$

where: A_o is the average recorder signal for the sample solution, b is the signal at the non-absorbing line, i is the number of the addition, and A_i is the average recorder signal after the i^{th} addition of beryllium, and W is the sample weight in grams.

(2) Calculate the final value as the average of the three values. The small volumes added to and removed from the sample solution during the analysis may be neglected in the calculation. Since both sample and standard are prepared on a weight/volume basis, the calculation is independent of the actual dilution used. The 5-ml volumetric flasks were convenient for the procedure.

HGA-70 Procedure

Scope. This procedure is for the determination of 1.0–1000 ng Be/g in petroleum and petroleum products.

Outline of Method. The sample is diluted approximately 1:1 with tetrahydrofuran (THF) and analyzed using a standard addition technique and the Perkin-Elmer HGA-70 graphite atomizer.

Apparatus

(1) *Atomic absorption spectrometer.* Perkin-Elmer model 403, or equivalent instrument, equipped a strip chart recorder.

(2) *HGA-70 graphite furnace atomizer.*

(a) Grooved type furnace (Perkin-Elmer No. 040-6088).

(3) *Microliter syringe.* 100-μl syringe with a glass or plastic needle.

Reagents

(1) *Tetrahydrofuran.* Eastman Kodak Co.

(2) *1000 ppm Zirconium reference standard.* Aztec Instruments, Inc.

(3) *Conostan D-20 standard.* 500 μg/g of 20 elements in white oil (Continental Oil Co.).

(4) *10 μg/ml Standard.* Prepared by accurately diluting 1.00 gram of Conostan D-20 to 50 ml with tetrahydrofuran.

(5) *1.0 μg/ml Standard.* Prepared by diluting 1.0 ml of the 10 μg/ml standard to 10 ml with tetrahydrofuran.

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Procedure

(1) Accurately weigh 12.5 g of sample into a 25-ml volumetric flask and dilute to volume with tetrahydrofuran (THF).

(2) Attach the HGA-70 atomizer to the instrument.

(3) Install new cones and a new furnace in the atomizer.

(4) Adjust the instrument parameters using the following settings as a guide.

Wavelength	234.9 nm
Slit	4 (0.7 nm)
Instrument response	1
Atomization volts	10
Atomization time	50 sec
Charring time	up to 15 min (optimize for each sample)
Charring cycle	7
Furnace	Grooved type (Perkin-Elmer No. 040-6088)
Recorder	2 mv full scale
Background corrector	on
Lamp current	low enough to balance background coorector

(5) With a microliter syringe, place 100 μl of the 1000-μg/ml zirconium standard on the furnace and cycle through the three-stage heating cycle.

(6) Repeat Step 5.

(7) With a syringe, quantitatively place 100 μl of the diluted sample prepared in Step 1 on the furnace and initiate the three-stage heating cycle.

(8) Start the strip chart recorder about 30 sec before the atomization cycle is initiated, and record the signal until the end of the atomization cycle.

(9) Repeat Steps 7 and 8 three times (or until a reproducible signal is obtained). This is signal A_0. With some types of samples the beryllium signal may not be reproducible for the first few injections. However, after five to 10 injections the signal should stabilize and be reproducible to within 10% for subsequent determinations.

(10) With a syringe add 100 μl of the 1.0 μg/ml standard (100 ng Be) to the sample flask and mix well.

(11) Again record the responses obtained from three 100-μl aliquots of the sample. This is signal A_1.

(12) Repeat Steps 10 and 11 two more times and record signals for 200 and 300 μl of Be as A_2 and A_3.

(13) Record a furnace blank signal by cycling the furnace through the heating cycles without a sample in the furnace.

Measurement of Beryllium Response from Strip Chart Recorder

(1) With a scale, measure the distance (a) between the maximum of the beryllium peak of signal A_3 and the termination of the atomization cycle, (Figure 6.4).

(2) Establish the furnace blank (b) at the beryllium peak maximum by measuring the response at the same distance (a) from the termination

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of the atomization cycle as the maximum beryllium response is from the termination of the atomization cycle, (Figure 6.4).

(3) Establish the total response (c) by measuring the distance from the beryllium peak maximum to the base line.

(4) Establish the beryllium response by subtracting the furnace response (b) from the total response (c).

(5) Determine the beryllium response for each measurement at A_0, A_1, A_2, and A_3.

(6) Average the three beryllium responses at each of A_0, A_1, A_2, and A_3.

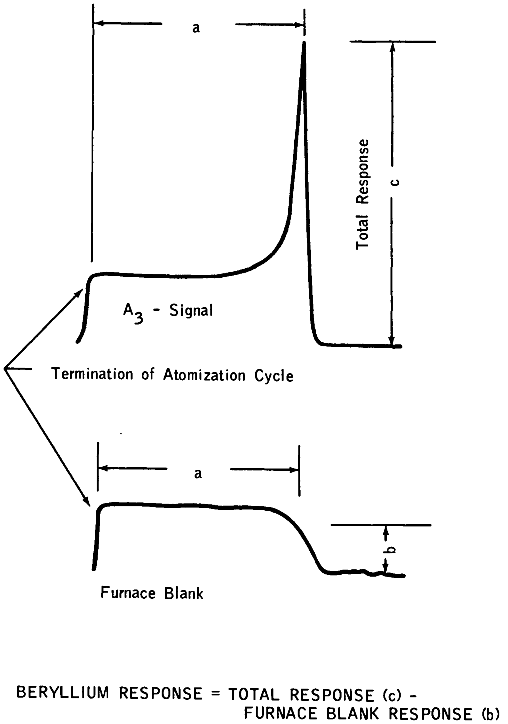

Figure 6.4. Determination of beryllium response

Calculation of Beryllium Concentration in Original Sample

(1) Calculate the beryllium concentration after each standard addition as follows:

$$\text{ng Be/g} = \frac{\text{total nanograms added}}{\text{sample weight}}$$

(2) Plot the beryllium response vs. ng Be/g added and draw the best straight line through the series of points. Assuming a sample size of 12.5 g, the points to be plotted are as follows:

$$\text{Signal } A_0 \quad \text{vs.} \quad \text{ng Be/g} = 0.0$$

$$\text{Signal } A_1 \quad \text{vs.} \quad \text{ng Be/g} = \frac{100}{12.5} = 8$$

$$\text{Signal } A_2 \quad \text{vs.} \quad \text{ng Be/g} = \frac{200}{12.5} = 16$$

$$\text{Signal } A_3 \quad \text{vs.} \quad \text{ng Be/g} = \frac{300}{12.5} = 24$$

If the points do not fall on a straight line, it suggests that the furnace heating characteristics changed during the time that the measurements were taken, and the sample must be re-analyzed.

(3) Extrapolate the line through the series of points until it intersects the ng Be/g axis. The ng Be/g at the point of intersection is the beryllium concentration in nanograms/gram in the original sample (*see* Chapter 3, Standard Additions).

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7

Cadmium

Cadmium is among the metallic elements included in the EPA atmospheric monitoring program (*1*), and standards have now been set for emissions. In New York city, a limit of 0.15 $\mu g/m^3$ has been established for industrial stack emissions (*2*). A matter of some concern, therefore, is the possible presence of minute traces of cadmium in petroleum-derived fuels. Consequently, analytical methods for measuring the concentration at the part-per-billion level were investigated.

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Available Analytical Methods

Cadmium has been determined in macro quantities by conversion to the sulfate, usually after separation as the sulfide, or as the pyrophosphate (*3*). Electrolytic methods, in which cadmium is plated on a cathode, have been used (*4*). Chelometric titrations that combine pH control with various complexing agents to eliminate interfering elements (*5*), using reagents such as dithizone and 8-quinolinol, have been popular for milligram amounts of cadmium. Colorimetric methods based on the use of dithizone or di-β-naphthylthiocarbazone have been widely used for traces of cadmium (*6*). Complexing reagents and pH-controlled extractions have been used to control interferences and to make these colorimetric methods quite sensitive and specific; however, their applicability to the trace levels of concern in petroleum is questionable. Electrochemical methods are capable of determining traces of cadmium in the presence of zinc, which may be present in petroleum and with which cadmium is often associated (*4*).

In recent years atomic absorption has received most of the attention for cadmium determination because of its high sensitivity for the element and the absence of interferences (*7, 8*). The introduction of heated vaporization atomic absorption (HVAA) has extended the detection limit to picogram levels (*9, 10*).

The Trace Metals Project investigated both flame and heated vaporization atomic absorption. These studies included an evaluation of decomposition techniques and ultimately a program of independent cross-checks of the methods that were devised.

In Analysis of Petroleum for Trace Metals; Hofstader, R., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1976.

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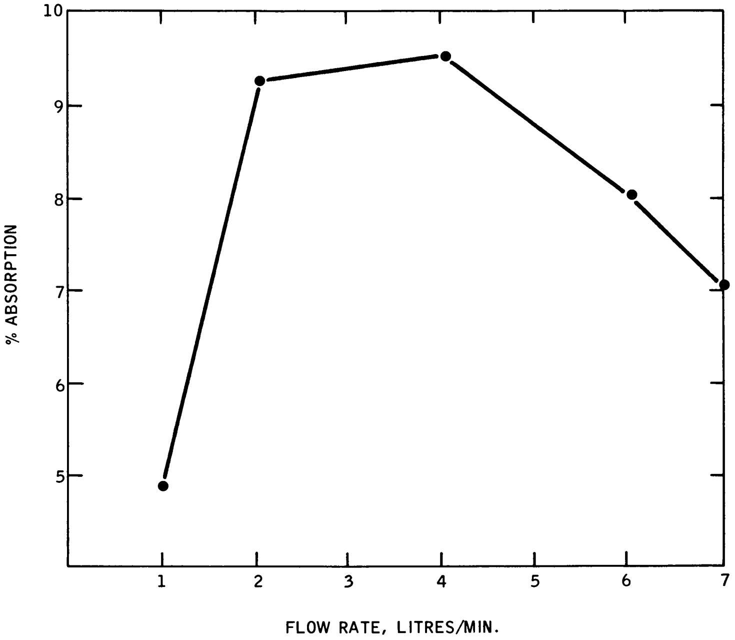

Figure 7.1. Effect of flow rate of N_2 on the absorption of 1 ng Cd/g

Role of Neutron Activation

Values for cadmium in petroleum and fuel have been reported by neutron activation (*11*). The technique is complicated by radionuclide interferences, however, and requires ashing, isotope dilution and separation techniques. Direct determination by the $^{114}Cd(n,\gamma,\beta)^{115m}$ reaction is theoretically possible, but extended irradiation and counting times are required, and it is difficult to reach the nanogram/gram level. The principal gamma particle, 336 KeV, is subject to interference from the ^{24}Na double escape peak at 346 KeV if the sample is high in sodium or if a low resolution detector is used.

Special Analytical Considerations

The stability of cadmium standards has been discussed in Chapter 2. During studies with known blends, low recoveries were obtained on petroleum samples that had been spiked with cadmium cyclohexanebutyrate several weeks earlier. To confirm this apparent loss, portions of a gasoline were spiked at the 30-ng/g level with cadmium cyclohexanebutyrate and cadmium sulfonate. The samples were stored in polytetrafluoroethylene (Teflon) bottles and were analyzed over a period of a month. Recovery from the samples spiked with cadmium cyclohexanebutyrate gradually decreased over the period of study, but the added cadmium was completely recovered from the samples spiked with cadmium sulfonate (Figure 7.1). Blends for long range studies were, therefore, prepared with the sulfonate.

Sample Preparation

Serious cadmium losses have been reported when organic samples were ignited and ashed by the dry-ash method (*12*). This was confirmed during work of the Project. A sample of spiked crude oil was ignited to a carbonaceous residue, and the carbon was burned off in a muffle furnace after the residue was wetted with a few drops of sulfuric acid. The inorganic ash was solubilized with dilute hydrochloric acid and then was analyzed by flame atomic absorption. Recovery of added cadmium averaged 78%.

Three alternate techniques yielded quantitative recovery of cadmium from various matrices: acid digestion (wet oxidation), ashing in the presence of sulfuric acid (wet ash), and a scaled down wet ashing procedure (mini-ash). The mini-ash technique is designed for small samples and is well suited for HVAA analysis.

Wet Oxidation. Several grams of sample are oxidized in a Kjeldahl flask with sulfuric and nitric acids. Heat is applied with a burner or heating mantle, and more acid is added as the oxidation progresses. This technique gave quantitative recovery from various petroleum matrices, but it is rather lengthy and requires constant attention. Troublesome frothing frequently occurs during acid addition, and large volumes of reagents are needed, increasing the possibility of high blanks.

Wet Ash. Up to 100 g of sample is mixed with concentrated sulfuric acid and ashed in a Vycor beaker. The beaker is placed in an air bath, and heat is applied from a hot plate and a heat lamp. The carbonized sample is then ashed in a muffle furnace, and the ash is dissolved in dilute hydrochloric acid. This technique is also lengthy, but unlike acid digestion it requires little attention; it can also accommodate large samples, and reagent blanks are nominal. This method of sample preparation was adopted for the measurements made by flame atomic absorption.

Mini-Ash. Up to 1 g of sample is wet with concentrated sulfuric acid in a Vycor crucible. The sample is oxidized by gradually increasing the heat from a hot plate and a heat lamp, and it is then ashed in a muffle furnace. The ash is dissolved in 2 ml of dilute hydrochloric acid. This technique uses a minimum volume of acid and is, therefore, less likely to become contaminated with traces of cadmium. It was adopted for the measurements made by HVAA, where the quantity of analyte that is needed may be as little as a few picograms.

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Measurement

Flame Method. CHOICE OF BURNERS. The response obtained on aqueous cadmium solutions with a force-fed total consumption burner was compared with that obtained with a Techtron partial-consumption burner. The operating conditions were adjusted to give the leanest possible flame, yielding maximum sensitivity. Both burners gave linear response. The total-consumption burner gave a greater response than the partial-consumption burner, but it caused considerable spectral noise, resulting in poorer precision and offered no improvement in detection limit Table 7.I). It also produced a disturbing amount of audible noise.

Table 7.I. Detection Limits and Sensitivities for Cadmium

	Sensitivity,[a] ng Cd/ml/1% abs	*Detection Limit,[b] ng Cd/ml*
Cd in 0.6*N* HCl		
partial-consumption burner	22	5
total-consumption burner	5	5
Cd in gasoline		
partial-consumption burner	12	5

[a] Sensitivity is defined as ng Cd/ml for 1% absorption.

[b] Detection limit is defined as concentration in ng Cd/ml that produces an absorbance equal to twice the magnitude of the fluctuation of the blank or background noise.

RESPONSE IN HYDROCARBON VS. AQUEOUS SOLUTION. To evaluate the possibility of determining cadmium directly in petroleum products by flame analysis, a gasoline sample was spiked with varying amounts of cadmium cyclohexanebutyrate, and the absorbance from each solution was measured with the partial-consumption burner. The response was greater than with aqueous solutions, but the detection limit remained about the same. Although a direct flame measurement for cadmium could be carried out on gasoline at the 5-ng/g level, it could not be applied to heavier petroleum fractions and crude oils, which would require dilution to a less viscous matrix before they could be analyzed. All subsequent flame measurements were with aqueous solutions.

INTERFERENCES. Cadmium compounds dissociate readily in the flame, and it has been reported that there are no major interferences (*13*). Nonspecific absorption, measured at the 226.7-nm Cd line, was insignificant in all the matrices studied.

Heated Vaporization Method. Heated vaporization atomic absorption (HVAA) utilizing a carbon rod or furnace has been discussed in Chapter 2. The technique has a sensitivity advantage for cadmium amounting to several orders of magnitude. Although HVAA is more

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exacting than conventional flame analysis, it has proved to be reliable in the hands of an experienced analyst. It requires only a few microliters of sample for the actual measurement, making it advantageous where the quantity of sample is limited. In petroleum analysis, the quantity of sample is not usually a problem. A small sample, however, has the advantage of minimizing contamination by its use of reduced amounts of reagents and shorter ashing times. A Varian-Techtron CRA-63 was used in the work carried out in the Project (*14*).

RESPONSE OF CRA-63. The most reproducible absorbance signals for cadmium are obtained with a power setting of 4 for 7 sec. During the atomization at this setting, the power gradually increases to 0.33 kW and gives smooth, reproducible signals. At settings above this, the tube is heated past the atomization temperature for cadmium so rapidly that the signal is limited by the detector–recorder response factors. Detector-limited response results in a non-linear calibration curve.

Care must be exercised during the ashing cycle or cadmium will be volatilized prematurely and the atomization signal will be reduced. If the setting is too low, however, longer ashing times will be required to remove the sulfuric acid completely.

Nitrogen or argon is used as a sheathing gas to retard oxidation of the furnace. A rate of 4 liters/min gives adequate protection and reproducible signals for cadmium. The rate of gas flow, however, has a significant effect on the cadmium response, with maximum response at 3–4 l/min.

DIRECT ANALYSIS VS. ASHING. The direct procedure, involving injection of non-aqueous solution into the furnace, was applicable to volatile samples such as gasoline. However, the low boiling point of cadmium made it necessary to ash at a low temperature, and the cadmium signal could not be satisfactorily separated from background continuum absorption when analyzing heavier matrices such as white oils, crudes, or residua (*14*). To overcome this problem, the carbon cup (*15*) was substituted for the furnace. However, the oil wet the graphite and "crept" up the sides of the cup to the cooler regions during the pre-atomization step, and the sample was not completely decomposed. Use of ashing acids such as sulfuric acid, ammonium persulfate, and benzene sulfonic acid offered no improvement, even when the sample was heated very gradually. These difficulties led to selection of external ashing.

MATRIX EFFECTS. Despite adoption of an ashing pretreatment sensitivity varied with the composition of the original sample (Table 7.II). Variable response is probably related to the presence of salts not atomized at the relatively low temperatures used. After the first few injections, the decreased response caused by salt buildup stabilizes, the magnitude of the decrease depending on the sample. Salts can be removed by high-

Table 7.II. Effect of Matrix on the Determination of Cadmium by HVAA Mini-Ash Procedure

Sample	ΔA *per 1 ng/ml change in concentration* $(\times 10^3)$
Crude A	6.6
Crude C	6.4
Heating oil	13.2
Reagent blank	12.8

temperature treatment of the carbon furnace. To avoid interference by salts in the measurement, the method of standard additions was chosen.

Chloride has been reported to interfere with cadmium in HVAA techniques (*16*). However, with the proposed method the amount of chlorine remaining after the prescribed sulfuric acid treatment is not sufficient to cause a problem.

Recommended Methods

The studies described above were carried out in two laboratories and led to the adoption of two separate methods.

Wet Ash-Flame Atomic Absorption. A sample, selected to provide an estimated 100 ng of cadmium, is charred to a carbonaceous residue in the presence of 5 ml of concentrated sulfuric acid. The residue is burned to an inorganic ash in a muffle furnace and dissolved in 10 ml of dilute hydrochloric acid. The acid solution is then aspirated into the flame (air–acetylene), and the absorption is measured. The cadmium content of the solution is obtained from a calibration curve.

The accuracy of the method was evaluated by adding known amounts of cadmium (as the sulfonate) to samples of a crude oil, a gasoline, and a No. 6 fuel oil, which had all been previously found to contain no cadmium when analyzed by the method. The results, shown in Table 7.III, indicate quantitative recovery and the absence of interferences.

Table 7.III. Recovery of Cadmium by Proposed Method

	Cadmium Concentration (ng/g)	
Sample[a]	*Added*	*Measured*
Gasoline	1.0	2.2, 2.4
No. 6 fuel oil	10	12
Nigerian crude	10	8, 12
	20	21
	40	39

[a] < 2 ng/g found in unspiked sample in all cases.

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As a further check on the method, a gasoline, a jet fuel, and a crude oil were each "spiked" with approximately 30 ng/g of cadmium (as the sulfonate) and analyzed in three different laboratories. The average recoveries (corrected for blank recoveries on the unspiked oils where necessary) are shown in Table 7.IV, which also includes data by the mini-ash–HVAA method. The individual data have been previously reported, along with a comprehensive statistical analysis (*14*). There are several discrepancies with the crude oils, more so than with the finished products, that may represent sample inhomogeneity. Nevertheless, the agreement between laboratories is considered acceptable at these low levels, and the overall recovery indicates accuracy within the established precision limits.

Mini-Ash–HVAA. A 0.5-g sample is treated with sulfuric acid, ashed at 525°C in a muffle furnace and taken up in dilute acid. At a fixed time interval, 1-μl portions of the acid solution are injected into the carbon furnace. Successive 5-μl portions of a 1-μg/ml Cd standard are then added, and the average signal after each addition is recorded. The concentration of the cadmium in the original sample is calculated from the standard additions data.

The accuracy of the HVAA part of this method was evaluated from the recovery of known amount of cadmium added to acid digests from various petroleum products. In this case a Kjeldahl digestion procedure was used. The results, shown in Table 7.V, indicate that the HVAA part of the procedure was accurate and applicable to digests from different petroleum matrices. However, the Kjeldahl digestion procedure gave low recoveries if the cadmium was added before the sample was decomposed.

As a preliminary test of the accuracy and precision of the complete method as recommended, a crude oil, that was found to contain less than 10 ng/g of cadmium when tested by the method, was spiked with 26 ng/g of cadmium and analyzed 10 times. The mean recovery was 28 ng/g, with a standard deviation of 6 ng/g. As in the case of the wet ash–flame method, additional accuracy and precision data were obtained by cross-checks in three different laboratories (*14*). The results, also consolidated in Table 7.IV, confirmed the validity of the method.

Wet Ash–Flame Atomic Absorption Procedure

Scope. This method is intended for the determination of cadmium in petroleum and petroleum products at levels as low as 10 ng/g. No interferences have been encountered.

Summary of Method. A sample estimated to contain 100 ng of cadmium is heated with 5 ml of concentrated sulfuric acid to a dry carbo-

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Table 7.IV. Interlaboratory Analysis

Cadmium Concentration (ng/g)

	Added	*Measured*			
				Lab 2	
Sample		*Flame*	*M-A*	*Flame*	*M-A*
Gasoline	28	30	—	27	—
Jet fuel	31	30	—	25	—
No. 2 heating oil	32	—	27	—	29
Crude A	32	—	36	—	29
Crude B	32	—	33	—	22
Crude C	29	39	—	40	—

[a] Omitted from overall average.

naceous ash. The ash is ignited to an inorganic residue and dissolved in dilute hydrochloric acid. The acid solution is made to volume, and the cadmium is measured by aspirating into an air–acetylene flame.

Apparatus

(1) *Atomic absorption spectrophotometer.* Jarrell-Ash model 82-546 spectrometer, equipped with Techtron laminar-flow burner and Sargent model SR recorder or equivalent. Any recorder having a range of 1-10 mv can be used. A digital concentration or absorbance readout is also acceptable.

(2) *Vycor dish.* An 800-ml beaker cut to a 10-cm height is convenient.

Table 7.V. Recovery of Cadmium by Kjeldahl Digestion—HVAA Method

	Cadmium Concentration (ng/g)	
	Added (as the Sulfonate)	*Measured*
Crude A	0, 0	0, 1
	10, 10	9, 13
	20, 20	20, 22
Light distillate	0	0
	10	10
	20	17
Middle distillate	0	1
	10	11
	20	22
Heavy distillate	0	9
	10	21

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for Cadmium by the Proposed Method

Cadmium Concentration (ng/g)

Measured				
Lab 3		*Lab 4*		
Flame	*M-A*	*Flame*	*M-A*	*Overall Avg.*
28	—	—	—	29
35	—	—	—	30
—	35	—	39	32
—	26	—	58[a]	30
—	18	—	43	34
18	—	—	—	32

(3) *Air bath,* constructed of aluminum so that the diameter is slightly larger than that of the dish and the height about 0.6 cm less than the dish.

(4) *Infrared lamp,* 250 watt, supported about 1.6 cm above the air bath. A variable transformer to regulate the heat of the infrared lamp is helpful.

(5) *Syringes,* 25- and 100-μl.

(6) *Volumetric flasks,* 100-ml polypropylene, and 10- and 25-ml borosilicate.

(7) *Muffle furnace,* capable of maintaining a temperature of 550° ± 25°C.

Reagents. Unless otherwise indicated, reagents are ACS reagent grade. All references to water mean distilled and deionized.

(1) *Sulfuric acid,* concentrated.

(2) *Hydrochloric acid,* concentrated.

(3) *Hydrochloric acid,* 0.6*N*. Dilute 5 ml of concentrated hydrochloric acid to 100 ml with water.

(4) *Aqueous cadmium standard,* 1000 ppm. Available from several suppliers.

Instrument Operation

(1) Set the instrument to measure cadmium using the following instrument and flame conditions as a guide:

Lamp current	5 ma
Analytical line	228.8 nm
Photomultiplier	UV sensitive
Band pass	as recommended for instrument
Burner head	air–acetylene
Gas flow rates	6.2 SCFH C_2H_2, 17.5 SCFH air
Nebulization rate	1.5 ml/min
Read out	absorbance or concentration

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(2) Optimize the instrument for maximum sensitivity according to the manufacturer's instructions.

(3) Adjust the air–acetylene ratio for the leanest possible flame.

(4) Adjust the burner height while aspirating a cadmium standard to the most sensitive setting.

Standardization

(1) *Preparation of calibration standards.* Add 1, 2, 3, 5, 10, 15, and 20 μl of the aqueous cadmium standard to separate 100-ml polypropylene flasks and dilute to volume with 0.6*N* hydrochloric acid. These solutions contain 10, 20, 30, 50, 100, 150, and 200 ng Cd/ml.

(2) *Calibration.* Adjust the base line to zero absorbance while aspirating 0.6*N* hydrochloric acid. Aspirate each standard cadmium solution in turn and record the reading. Plot the readings obtained against cadmium concentration.

Procedure

(1) *Sample decomposition.*

(a) Weigh the sample (100 g maximum) into a Vycor dish. Add 5 ml of concentrated H_2SO_4, mix with a glass stirring rod, and place the dish in an air bath. At the same time, start a reagent blank with 5 ml of H_2SO_4.

(b) Place the bath on a hot plate and suspend an infrared lamp above it so that the face of the bulb is 0.6 to 1.2 cm above the top of the dish. Decompose the sample, slowly at first, with heat from the lamp, and then with low heat from the hot plate. Stir frequently with a glass rod to break up the surface crust to reduce spattering. Use a face shield.

(c) When H_2SO_4 fumes are no longer evolved, transfer the dish to a muffle furnace at 550°C, and heat until all organic matter has been burned off.

(d) Cool, wash down the walls of the dish with 10 ml of 0.6*N* HCl, cover the beaker, and dissolve the ash by warming on the steam bath. Transfer the solution to a 10-ml volumetric flask, diulte to volume with 0.6*N* HCl, and mix thoroughly.

(2) *Atomic absorption measurement.*

(a) Check the calibration of the instrument (Step 2 under *Calibration*) just before analyzing the sample solutions.

(b) Aspirate the reagent blank and sample solutions and record the absorbance.

Calculation

(1) Convert the absorbance to nanograms of cadmium by referring to the calibration curve.

(2) Calculate the cadmium concentration of the sample as follows:

$$\text{ng Cd/g} = \frac{V(A - B)}{W}$$

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where:

A = ng Cd/ml in prepared sample solution.
B = ng Cd/ml in blank.
V = final volume of solution (10 ml).
W = sample weight, grams.

Wet Ash-Heated Vaporization Atomic Absorption Procedure

Scope. This method is intended for the determination of cadmium in petroleum and petroleum products at levels down to 10 ng/g. The presence of other metals affects the atomic absorption signal, but the effect is overcome by using a standard additions technique.

Summary. The sample (usually 0.5 g) is decomposed by treatment with 5–10 drops of concentrated sulfuric acid in a Vycor crucible and ignited to an inorganic ash. The ash is obtained as a solution in 1*N* sulfuric acid, which is injected into a heated graphite furnace. The atomic absorption signal from the sample solution, and from the sample solution plus several standard additions, is used to calculate the cadmium content of the sample.

Apparatus

(1) *Atomic absorption spectrometer.* Jarrell-Ash 82-500 or equivalent.

(2) *Recorder,* 0-10 mv full-scale. Any recorder having full-scale response of 0.5-second or faster can be used.

(3) *Carbon Rod Analyzer,* Varian-Techtron model 63 or equivalent.

(4) *Carbon furnaces and support electrodes,* supplied for the CRA-63 by Varian.

(5) *Muffle furnace,* capable of maintaining 550° ± 25°C.

(6) *Vycor crucible,* 30 ml.

(7) *Infrared lamp,* 250 watt. A variable transformer to regulate the heat of the infrared lamp is helpful.

(8) *Syringes,* 1- and 5-μl.

(9) *Teflon or polyethylene tubing,* No. 28. Cut into 2.5-cm lengths to fit over the syringe needle.

Reagents. Unless otherwise indicated, reagents are ACS Reagent Grade. All references to water mean distilled and deionized.

(1) *Sulfuric acid,* concentrated.

(2) *Sulfuric acid,* 1*N*. Dilute 27.8 ml of concentrated sulfuric acid to a liter of water.

(3) Hydrochloric acid, 6*N*. Dilute concentrated acid with an equal volume of water.

(4) Aqueous cadmium standard, 1000 ppm. Available from several suppliers.

Instrument Operation

(1) Set the instrument to measure cadmium, using the following conditions as a guide.

Lamp current	5 ma
Slit width	100 μ entrance 150 μ exit
Band pass	0.2 nm
Analytical line	228.8 nm
Background	226.7 nm
Photomultiplier	UV sensitive

(2) Set the CRA-63 control box using the following settings as a guide to the optimization of individual units:

Atomization tube	pyrolytic coated graphite
Support electrodes	FX 9 graphite
Inert gas	nitrogen (4 l/min)
Cooling water	4 l/min
Injection frequency	90 sec
Sample size	1 μl

CRA-63 Program	*Supply Setting*	*Power, kW*	*Seconds*
dry	3.5	0.004	15
ash	5	0.07	15
atomize	4	0.30	7

Recorder:	Speedomax W	(Leeds & Northrup or equivalent)
time constant	0.5 sec	
scale expansion	2.5X	
Read out:	peak height	

(3) Place a graphite atomization tube and two support electrodes in the workhead of the CRA-63. Adjust the instrument to give zero absorbance.

(4) Adjust the conditions so that a minimum tube blank is obtained

Procedure

(1) *Sample Decomposition*

(a) Weigh 0.50 ± 0.05 g of sample (for expected concentrations up to 25 ng/g) directly into a 30-ml Vycor crucible, and add 10 drops of concentrated H_2SO_4. At the same time, start a reagent blank.

(b) Place the crucible on a hot plate set at low heat. Suspend an infrared lamp 10-cm above the surface of the hot plate. Gradually increase the heat at a rate sufficient to avoid spattering, and heat until the evolution of sulfuric acid ceases.

(c) Transfer the crucible to a muffle furnace, and heat at 550°C until the carbonaceous matter is destroyed.

(d) Cool, add 1 ml of 6*N* HCl to the crucible, and heat to incipient dryness. After cooling again, add 1.0 ml of 1*N* H_2SO_4 and rotate the crucible so that the walls are wetted.

(e) Inject a 1-μl aliquot of the sample solution into the graphite tube, atomize the sample, and record the signal. If the signal is greater than 50% of recorder scale, dilute the solution with 1*N* H_2SO_4 and work with a 1-μl aliquot of both sample and blank.

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(f) Measure the absorbance on three 1-μl aliquots of the sample solution. If each of the three signals falls within 10% of their average, use that average. Otherwise, measure the absorbance twice more and calculate the average of the five signals.

(g) Measure the average signal in the same manner (three or five measurements) for each of three successive additions of 5 ng Cd, made by adding 5 μl of a 1-μg Cd/ml calibration standard to the sample solution.

(h) After the final addition, measure the background absorbance for each sample at the 226.7 nm non-absorbing cadmium line.

Calculation

(1) Calculate the apparent concentration of cadmium in the sample after each addition by the equation:

$$\text{ng Cd/g} = \frac{A_O - B}{W} \times \frac{(5\ \text{ng})\ (i)}{A_i - A_O}$$

where:

A_O is the average recorder signal for the sample solution.
B is the signal at the non-absorbing line.
i is the number of the addition (1, 2 or 3).
A_i is the average signal after the i^{th} addition of cadmium.
W is the weight of sample, in grams.

(2) Average the three values obtained.

(3) Measure the absorbance of the reagent blank in the same manner as the sample and calculate the concentration of cadmium in the blank by assuming a 0.5-g sample. Subtract this concentration of cadmium from the average amount found in the sample and report the difference as the cadmium content of the sample.

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8

Chromium

Chromium has been found in surveys of metals in crude oils, although its concentration rarely exceeds 1 ppm (μg/g) (*1, 2, 3*). In its native form, chromium is not particularly volatile and may be concentrated in the bottom fractions during refining (*2*). Chromium may also enter petroleum matrices as antioxidants added to jet fuels, as corrosion products, or as a wear metal in used lubricating oils. Although its ultimate fate is unknown, chromium may enter the atmosphere during the combustion of fuels or it may enter natural waterways as part of industrial effluents.

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Available Analytical Methods

A number of methods exist for the determination of parts-per-billion (ng/g) levels of chromium in aqueous media (Table 8.I). These are repeatedly reviewed as new techniques are introduced (*4, 5, 6*). Potentially all these techniques could be applied to petroleum samples after matrix destruction, but in practice, only a few have been utilized. After wet oxidation of a large sample ($>$ 100 g), 10 to 50 μg of chromium may be determined by a colorimetric procedure with 1,5-diphenylcarbohydrazide after iron, copper, molybdenum, and vanadium are extracted as the cupferrates (*3*). In survey analyses, Cr levels as low as 5 ng/g have been measured by optical emission spectroscopy after ashing (*2, 3*) or directly by neutron activation with extended irradiation and counting times (*1*). Concentrations of chromium above 100 ng/g in used lubricating oils have been measured directly by flame atomic absorption (*8*); for lower concentrations, heated vaporization atomic absorption (HVAA) has been utilized (*9*). In the Trace Metals Project, two procedures using this latter technique were evaluated for the determination of 10 ng Cr/g in a variety of petroleum matrices.

Special Analytical Considerations

Both ashing and acid digestion may be used to mineralize organic matrices containing chromium. Although chromium itself is not volatile, pretreatment with sulfuric acid aids in destruction of the hydrocarbon matrix (*10*). In initial ashing studies carried out by the Project, large

In Analysis of Petroleum for Trace Metals; Hofstader, R., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1976.

Table 8.I. Existing Techniques for Determining ng/g Levels of Chromium in Aqueous Media

Chemical	*Instrumental*
Extraction/colorimetry	Coulometric titrimetry
Catalytic kinetics	Differential pulse polarography
Chemiluminescence	Flame atomic absorption (solvent extraction)
	Gas chromatography (electron capture detector) (mass spectrometry)
	Heated vaporization atomic absorption
	Mass spectrometry (direct injection)
	Neutron activation
	Optical emission spectroscopy
	X-ray fluorescence (ion exchange)

variable blanks were found (*see* Contamination, p. 14). These blanks were attributed to exposed nichrome heating elements, since they could be almost completely eliminated by ashing samples for a minimum period in a muffle with covered elements.

Sample Preparation

Two procedures based on HVAA have been evaluated by the Project. In one, the sample is analyzed directly after dilution with tetrahydrofuran. In the other, a 0.5-g sample is charred with 10 drops of sulfuric acid in a 30-ml Vycor crucible and treated at 540°C for the minimum time required to remove carbonaceous deposits. The ash is then solubilized in 1*N* sulfuric acid prior to measurement. A reagent blank is carried through the procedure for each set of samples. The analyses are carried out promptly after preparation so that loss of chromium from aqueous solution by adsorption on the walls, which has been reported in some cases (*11*), can be avoided.

Measurement

Before analyses were carried out by the two procedures, the optimum HVAA parameters were established empirically using 20-ng/ml aqueous standards. HVAA measurements for chromium were made with a Varian Techtron CRA-63 atomizer; other tube furnace atomizers which possibly could have been used, were not investigated. Although the HVAA response was linear between 0–400 ng/ml, a working range of 0–50 ng/ml was utilized. The detection limit ($S/N = 2$) was calculated to be 1 pg. The absorbance of the neon 359.4-nm line in the chromium hollow cathode lamp was used to make background corrections.

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Chemical matrix effects were encountered in the HVAA determination. When a constant amount of chromium was added to different petroleum samples, the atomization response varied considerably from that obtained in THF alone (Table 8.II). Since almost parallel effects were noted after ashing, the effect of Fe, Ni, and V was studied. Excesses of vanadium had a significant effect at levels which often occur in crude oils (10 to > 100 ppm). Once vanadium was introduced in the atomizer, the chromium signal was consistently suppressed until the atomization furnace was baked at maximum temperature to remove residual vanadium.

From the data in Table 8.II it is apparent that components other than vanadium affect the chromium signal. No explanation has been found for the enhancement observed in some cases. Since a linear response is obtained after the initial injection of a given sample solution, the method of standard additions can be applied to compensate for these chemical matrix effects.

Recommended Method

In the direct HVAA procedure the sample is diluted with tetrahydrofuran. The concentration of chromium is determined by the method of standard additions coupled with background corrections if necessary.

This procedure has been applied to several crude oil samples, and the results were compared to those obtained by HVAA after sulfated ashing (Table 8.III). The good agreement between techniques verifies that no chromium is lost prior to atomization in the direct technique. Furthermore, it demonstrates that the combination of standard additions and correction for reagent blank and background overcomes the inter-

Table 8.II. Effect of Matrix on the Determination of Chromium by the Direct HVAA and Ash–HVAA Procedures

	$\Delta A \times 10^3$ *per ng Cr/ml Added*		*Crude/Solvent Ratio (Response Ratio)*	
	Direct (THF, 1:1)	*Ash (1N H_2SO_4, 5:1)*	*Direct*	*Ash*
Reagent Blank (THF)	0.99	5.63	—	—
Crude A	1.33	7.85	1.34	1.39
Crude B	1.20	7.07	1.21	1.25
Crude C	0.83	6.04	0.84	1.07
Crude D	0.42	5.57	0.43	0.98
Crude E	0.77	6.57	0.78	1.17

ferences encountered in the HVAA measurement. The sulfated ash procedure may be used to obtain reliable data, but the direct technique is simpler, has smaller reagent blanks, and is less subject to contamination. Consequently, the direct HVAA procedure, which has been evaluated by the cross-check program, is preferred.

The precision of the direct procedure was evaluated for a variety of matrices in the initiating laboratory. A base kerosene, which contained no detectable chromium, was spiked with 47.9 ng Cr/g as chromium naphthenate. The other samples contained native chromium. The results are shown in Figure 8.1, where the average values are represented by the points and the total spread of data by the brackets. The percentages given are relative standard deviations, and the degrees of freedom ($n - 1$) are given in parentheses. From the data shown the overall RSD in the initiating laboratory was 17%.

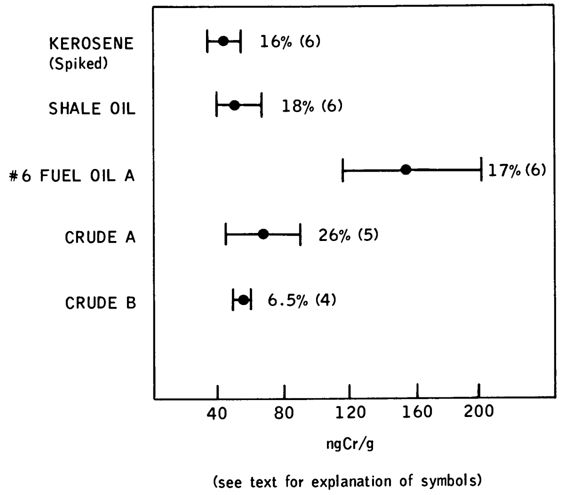

Figure 8.1. Intralaboratory data for determination of chromium

Four samples were analyzed in the cross-check program. The results obtained at the initiating lab and at two cooperating laboratories are summarized in Figure 8.2. The kerosene sample was used in the intralaboratory study. The arrow indicates the detection limit in the base kerosene; otherwise the symbols are the same as in Figure 8.1. For the kerosene and the shale oil, the RSD was 25% while for the No. 6 fuel oil it was 13%. Some scatter was encountered with the No. 6 fuel oil; this is attributed to difficulty with background corrections, since both a negative baseline and the background peak for this heavy matrix were involved. However, the average value obtained by the direct procedure was 145

Table 8.III. Comparison of Chromium by Two Procedures

	Chromium Concentration (ng/g)	
Sample	*Direct HVAA*	*Mini-Ash–HVAA*
Crude A	44, 77, 75, 90, 77, 49	57, 73, 61
Crude B	50, 56, 58, 59, 54	44, 61
Crude C	38	42, 49
Crude D	<.10	< 10, < 10
Crude E	108, 129	110, 93

ng/g. This compares favorably with the values which were obtained by the wet ash technique; by the latter method, the initiating laboratory found 126 ng/g, and two other laboratories reported values of 150 and 117 ng/g.

Detailed Procedure

Scope. The method is designed to determine chromium concentrations as low as 10 ng/g in petroleum and petroleum products. After setup, each sample requires about 30 min for analysis with this technique. However, sample preparation and apparatus setup limit output generally to 12 samples in one day.

Summary of Method. The sample is diluted with tetrahydrofuran, and the metal in the solution is measured with an atomic absorption spectrophotometer equipped with a carbon rod atomizer (CRA-63). The

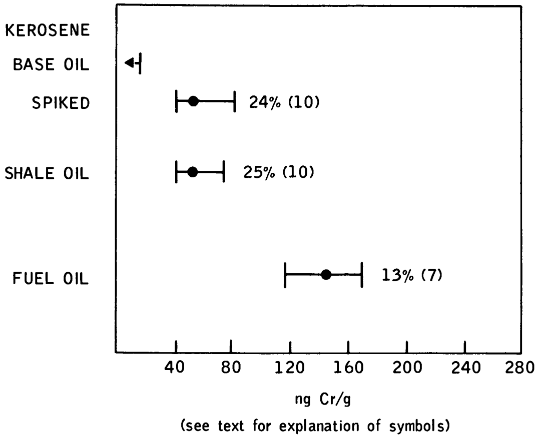

Figure 8.2. Interlaboratory data for determination of chromium

concentration of metal is calculated on the basis of changes in the absorption resulting from standard additions to the sample solution.

Apparatus

(1) *Carbon Rod Atomizer.* Varian Techtron model 63 or equivalent.

(a) 9-mm Pyrolytically coated atomization tube furnaces (Varian-Techtron).

(b) FX-91 Support electrodes (Poco Graphite).

(2) *Atomic Absorption Spectrophotometer* (*AAS*). (Jarrell-Ash, 82-500 series or equivalent).

(a) Strip chart recorder, 0-10 mv, with 0.5-sec response time (Leeds & Northrup Speedomax W or equivalent (*1*)).

(b) Chromium hollow cathode lamp (Westinghouse or equivalent).

(3) *Syringe,* with Teflon tip or Teflon needle, capable of delivering 5-μl samples reproducibly.

(4) *Micropipettes,* 5, 10, and 50 μl (capillaries, syringe or Eppendorf pipettor).

Reagents

(1) *Tetrahydrofuran* (*THF*) ACS reagent grade (Eastman, MCB).

(2) *Standards*

(a) Conostan, Cr standard, 5000 ppm (w/w) chromium-in-oil standard (Continental Oil Co., Ponca City, Okla.).

(b) Stock 1000 μg/ml standards. Weigh 2.0 g Conostan 5000 ppm (w/w) standard into a 10-ml volumetric flask and dilute to volume with THF.

(c) Calibration standard (5 μg/ml). Dilute 50 μl of 1000 μg/ml stock standard to 10 ml with THF.

Procedure. Initially all glassware must be cleaned with (1:1) nitric acid prior to use. The equipment is then rinsed several times with THF.

(1) Weigh 2.5 g of oil into a 5-ml volumetric flask and dilute to volume with the solvent.

(2) Optimize the HVAA for chromium with the tube furnace in the optics using the following settings as a guide.

Wavelength (nm)	357.8
Inert gas (l/min/psi)	N_2 7.5/10
Furnace	9 mm tube
Aliquot used	5 μl
CRA-63 Program	(*v/sec*)
dry	1.5/20
ash	6.5/30
atomize	9.5/3

The operating conditions for the CRA model 63 should serve only as guidelines. When the operating parameters are optimized, scale expansion should be used so that each 25 ng of metal in 5 ml solvent gives a response between 10 and 20 scale units. If the sample contains > 5× detection limit levels of the metals, the sample should be further

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diluted before standard additions. This dilution technique is recommended rather than changing operating parameters. The residual heat in the atomization tube contributes to the repeatability of sample signals. This effect may be minimized by injecting samples on a fixed schedule. For the method described here, injections made at 90-sec intervals give good repeatability.

(3) Aliquot 5 μl of the sample solution into the syringe, initiate the CRA-63 program, and immediately inject the sample.

(4) Record the absorbance peak height (A) observed during the atomization step.

(5) Repeat Steps 3 and 4 two more times; calculate the average peak height for each. If the three signals are within ± 10% of the average, use this value (A_0) in the calculation; if not, repeat the sequence of Steps 3 and 4 two more times and use the average of the five readings.

(6) Add 5 μl of the calibration standard (equivalent to 25 ng) to the sample solution, mix well, and carry out Steps 3–5. Record the average peak height as A_1.

(7) Add a second 5 μl of the calibration standard (25 ng, a total of 50 ng) to the sample solution and again carry out Steps 3–5. Record the average peak height as A_2.

(8) Add a third 5 μl of the calibration standard (25 ng, a total of 75 ng) to the sample solution and again carry out Steps 3–5. Record the average peak height as A_3.

(9) Reset wavelength to 359.4 nm and inject the sample solution (Step 8) to measure background. Record the reading as b.

Calculation

(1) Calculate the concentration of metal in the sample from the first addition as:

$$\text{ng/g Cr} = \frac{(25\text{ ng Cr})\text{ added}}{A_1 - A_0} \times \frac{A_0 - b}{2.5\text{ g}}$$

(2) Repeat the calculation for the second addition:

$$\text{ng/g Cr} = \frac{(50\text{ ng Cr})\text{ added}}{A_2 - A_0} \times \frac{A_0 - b}{2.5\text{ g}}$$

(3) Repeat the calculation for the third addition:

$$\text{ng/g Cr} = \frac{(75\text{ ng Cr})\text{ added}}{A_3 - A_0} \times \frac{A_0 - b}{2.5\text{ g}}$$

(4) Average the three values (from Steps 1, 2, and 3) and report that number as ng/g in the sample.

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9

Cobalt

Cobalt has been reported in the ppb range in surveys of crude oil metals content (*1, 2, 3*). The cobalt compounds in crude oils are relatively nonvolatile and are concentrated in the residual fractions during refining. Certain motor and heating fuels may contain traces of cobalt introduced in removal of mercaptans. Other fuels may contain traces of cobalt introduced in compounds used as combustion improvers to reduce smoke and soot formation.

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Available Analytical Methods

A number of instrumental methods have been used to determine ppb levels of cobalt in water (*4, 5, 6*), biological tissues (*7, 8*), and air particulates (*9, 10*). Kinetic methods are capable of measuring sub-parts-per-billion (*11, 12*). Potentially any of these techniques could be used in the analysis of petroleum, but only neutron activation analysis (*1, 3*) and atomic absorption spectroscopy (*13, 14*) have been applied to any appreciable extent. Flame and heated vaporization atomic absorption techniques were selected for more detailed study by the Project because atomic absorption is sensitive, subject to relatively few interferences, and is rather generally available.

Role of Neutron Activation. For determining cobalt by neutron activation, the ^{59}Co (n, γ) ^{60}Co reaction producing 1170 and 1330 KeV gamma ray peaks is used. With several hours of irradiation and long counting times, the technique is capable of measuring 5 ng Co/g. Nickel interferes by the reaction ^{60}Ni (n, p) ^{60}Co, which is induced by varying amounts of fast neutrons always present in the reactor; however, appropriate corrections can be made.

Sample Preparation

Two sample preparation procedures were used. In one, the sample is diluted with 1:1 xylene-quinoline or tetrahydrofuran, and the solution is analyzed directly by atomic absorption. A mixture of xylene and 4-methyl-2-pentanone (MIBK) can also be used as a diluent, but the xylene–quinoline mixture is a more effective solvent for residual fuels. Distillate fuels require no dilution.

In the other preparation procedure the sample is treated according to the method of Milner et al. (*15*). The method involves carbonization of the sample with sulfuric acid, ignition of the carbonaceous residue, and dissolution of the inorganic ash with dilute hydrochloric acid. No loss of cobalt was observed either during the decomposition or when the carbonaceous residue was ignited. There was no evidence of contamination from external sources during the decomposition, nor was there any detectable cobalt in the reagents.

Frequently, when crude oils and residual fuels were decomposed, an inorganic residue remained which was insoluble in dilute hydrochloric acid. However, tests showed that all of the cobalt was in solution, so the residue was ignored in subsequent steps of the determination.

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Measurement

Nonaqueous Solutions. Heated vaporization atomic absorption (HVAA), without preliminary decomposition, was evaluated. Nonaqueous solutions tended to creep over the surface and out of the furnace; this resulted in erratic and lower-than-expected absorption. To minimize creeping, samples were injected slowly over a 20-sec "dry" cycle into a warm furnace. The temperature of the furnace was kept low enough to avoid sputtering and consequent loss of sample but high enough to partially decompose the sample. With this injection procedure, absorption measurements were satisfactory for distillate fuels. However, even with a warm furnace and slow injection, creeping of these fuels could not be prevented when the amount injected was greater than 3 μl. Residual fuels and crudes not only required dilution, but also higher temperatures and longer atomization times to eliminate background and yield reproducible signals. The nonaqueous injection method, as evaluated, was the same as that recommended for chromium (*see* Chapter 8). With the maximum 3-μl injection, a detection limit of about 10^{-11} g was achieved. For distillate fuels (undiluted) this represents a detectable concentration of about 3 ng/g. For heavier stocks, the detectable concentration depends on the degree of enhancement or suppression of the signal by the other metals that are present.

Aqueous Solutions. Two measurement procedures for aqueous solutions were evaluated in the Project—atomic absorption (AA) with an air–acetylene flame and heated vaporization atomic absorption. Optimum parameters for both measurements were established empirically from the response for standard solutions of cobalt in dilute hydrochloric acid.

The response in the flame AA measurement was linear over the range of 0–5 μg Co/ml, and by starting with a 100-g sample as little as 5 ng Co/g could be determined in the original sample.

Table 9.I. Effect of Matrix on the Determination of Cobalt by HVAA

Concentration of Co in solution: *0.5 μg/ml*
Quantity injected: *1 μl*

Conc. of each metal,[a] *μg/ml*	*Avg. Response, mm*	*Number of Measurements*	*Std. Dev. of Response, mm*
0	46	6	4
0.5	48	3	2
5	56	3	3
50	52	3	2

[a] Interfering metals present: Si, Al, Cr, Pb, Cu, Fe, Mg, Na, Zn, Ca, V, Ni, Mo, and Mn.

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In the HVAA measurement, the power and time for the "ash" cycle were adjusted so that no cobalt was volatilized prematurely, and the power and time for the "atomize" cycle were adjusted until maximum absorption was obtained, with no "memory" from one atomization sequence to another. Background (non-atomic) absorption at the analytical wavelength of 240.7 nm was investigated using a hydrogen continuum lamp. The background signals were indistinguishable from the baseline.

Under these conditions, the detection limit ($S/N = 2$) in the measurement of cobalt by HVAA was 5×10^{-12} g. With this limit it was possible to determine Co down to the 1 ng/g level if a 100-g sample was ashed. Instrument response was linear over the range of 0–0.5 μg of Co.

The flame AA measurement for cobalt is reported to be relatively free of interferences (*16*). Results obtained on some typical samples (Table 9.IV) support this conclusion.

Little information has been available on interferences in the HVAA measurement. The effect of mixtures of 14 common metals on cobalt absorption by HVAA as determined by the Project is shown in Table 9.I.

Table 9.II. Interference of Common Contaminants on the Determination of Cobalt by HVAA

Concentration of Co in solution: *0.1 μg/ml*
Quantity injected: *5 μl*

Concn. of Interfering Metal, g/ml				*Avg. Response, mm*	*No. of Measurements*	*Std. Dev. of Response, mm*
V	*Ni*	*Fe*	*Na*			
0	0	0	0	50	14	5
0.4	0.2	0.05	0.05	58	9	4
4	2	0.5	0.5	68	8	5
40	20	5	5	58	9	4
400	200	50	50	44	8	5

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When all 14 metals were present, each at a concentration greater than that of the cobalt, the absorption was increased significantly. There was a similar and possibly greater effect when only V, Ni, Fe, and Na, the most common contaminants, were present (Table 9.II). Absorption appears to pass through a maximum as the ratio of interfering ion to cobalt increases. The reason for this is obscure, but enhancement could have resulted from the formation of a protective refractory carbide that increased the number of analyte atoms produced (*17*). The depression could have been caused by covolatilization of the cobalt with dry salt particles (*5*) or occlusion in the salt particles affecting the rate of atomization (*18*). Apparently both enhancement and depression effects can occur simultaneously, with the net response depending on both concentration and absolute amounts of cobalt and interfering metals. Despite this effect, the response for a given system was linear up to 100 ng Co/ml (Figure 9.1), allowing the method of standard additions to be used.

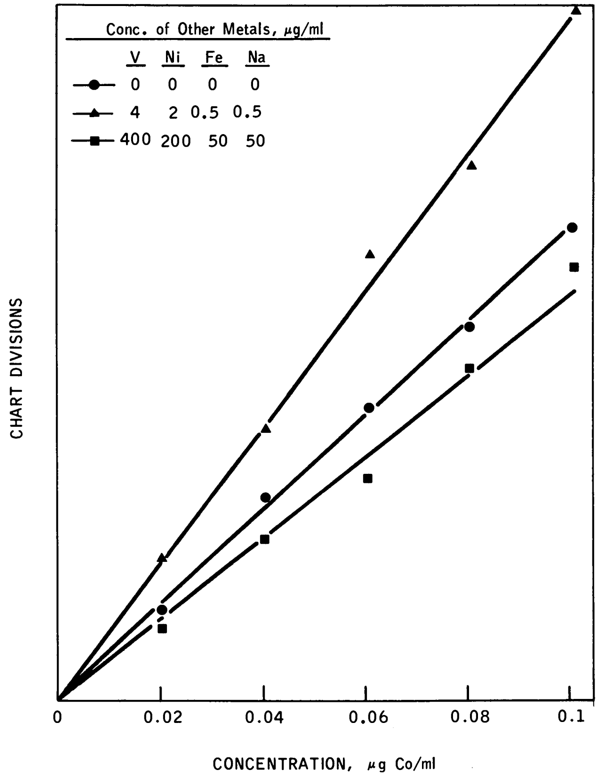

Figure 9.1. Effect of other metals on cobalt calibration curves

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Recommended Method

As a result of the work described above, three procedures proved acceptable: (1) nonaqueous HVAA; (2) wet ashing with flame AA finish; and (3) wet ashing with HVAA finish. Procedure (1) is probably the least subject to contamination, but it is recommended only for distillate fuels that do not need to be diluted. Procedure (2) avoids the time-consuming standard additions step, uses simpler equipment, and is applicable to all types of petroleum samples, but it requires a large sample to achieve the desired sensitivity, with a correspondingly lengthy decomposition step. Procedure (3) requires the same type of decomposition as (2) to make it generally applicable, but smaller samples can be taken and the final solution may be analyzed for several other metals (e.g., Cr, Mn, Mo, Ni, V) as well. Despite the need for standard additions, Procedure (3) was considered to be the preferred method and was the one chosen for cross-checking. Tables 9.III and 9.IV compare the results obtained at one laboratory using this method compared with those obtained using the other two methods.

In the recommended method, 1 g of sample is decomposed by heating with concentrated sulfuric acid. Larger amounts are taken if a detection limit of less than 10 ng/g is desired or if several elements are to be determined in the same final solution. The resulting carbonaceous residue is ashed in a muffle furnace at 500°C. The ash is dissolved in dilute hydrochloric acid, and the concentration of cobalt is measured by HVAA using the method of standard additions.

The recommended method was tested in both the originating and a cooperating laboratory on a crude oil, gasoline, jet fuel, and a No. 6 residual fuel. The gasoline and jet fuel were spiked with cobalt sulfonate. The residual fuel and the crude oil contained native cobalt and were not spiked. The cooperating laboratory analyzed each sample according to the procedure, without any knowledge of the cobalt content of the samples. The results are shown in Figure 9.2.

The vertical lines on the chart represent two standard deviations about the spike level for gasoline and jet fuel and about the mean of the results on the crude oil and residual fuel. Results between laboratories on the gasoline and the crude oil agreed within two standard deviations. While there is considerable scatter in the individual results on the No. 6 fuel oil, average results between laboratories agreed reasonably well. Only for jet fuel did the results differ significantly between laboratories.

It was suspected that some of the cobalt sulfonate added to the jet fuel had decomposed and the cobalt had plated onto the walls of the container before the cooperating laboratory had started the analysis. This type of loss, however, was not confirmed in a long-term stability study by neutron activation analysis, which showed that cobalt sulfonate was stable

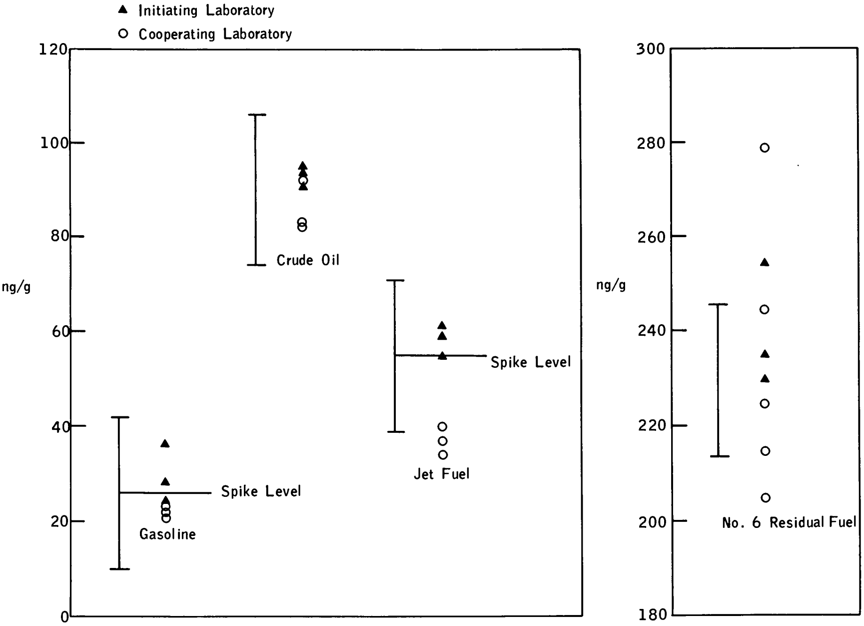

Figure 9.2. Determination of cobalt in petroleum by different laboratories: wet ash HVAA method

in both a typical crude oil and kerosene. Jet fuel is considered sufficiently similar to kerosene for the results of the long term stability study to apply. The explanation, therefore, does not account for the cooperating laboratory's low results on jet fuel. Nevertheless, the close agreement obtained on the crude oil and the No. 6 residual fuel, both of which contained naturally occurring cobalt, suggests that the difficulty was with the synthetically prepared jet fuel sample rather than with the method itself.

The within-laboratory standard deviation on these tests was ± 8 ng Co/g over the range of 0.0–250 ng Co/g. This precision was identical to that calculated from the data summarized in Tables 9.II and 9.III, as obtained by the initiating laboratory during the development of the method.

Detailed Procedure

Scope. The method is used for determining cobalt in petroleum and petroleum products at levels as low as 1 ng/g. Six to 12 samples can be processed conveniently in a batch, with a total working time of 8 hr.

Summary of Method. The sample (1–10 g) is decomposed by heating with sulfuric acid. The resulting carbonaceous residue is ashed in a muffle furnace at 500°C. The ash is dissolved in dilute hydrochloric acid and

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Table 9.III. Cobalt Concentration as Determined by Different Methods

	Cobalt Concentration (ng/g)		
	Added	*Measured*	
Sample		*Wet-Ash HVAA (n = 3)*[a]	*Direct HVAA (n = 1)*[a]
Gasoline	30	31	27
Jet fuel	59	58	54
No. 2 fuel oil	36	34	33

[a] *n* = Number of determinations.

diluted to 10 ml. The concentration of metal is measured on 2-ml aliquots of the digestate by heated-vaporization atomic absorption using the method of standard additions.

Apparatus

(1) *Atomic absorption spectrophotometer.* Varian-Techtron AA5 or equivalent.

(a) Strip chart recorder, 0-10 mv with 0.5-sec response time (Leeds & Northrup Speedomax W or equivalent).

(b) Cobalt hollow cathode lamp (Varian-Techtron or equivalent).

(3) *Carbon rod atomizer.* Model 63 (Varian-Techtron).

(a) Pyrolytic-graphite coated atomization furnaces (Varian-Techtron).

(b) Support electrodes manufactured by Ringsdorff-Werke, GMBH, type RW 0124 (Varian-Techtron).

(3) *Vycor dish.* Cut an 800-ml beaker to a 10–cm height. To reduce the cobalt blank it is recommended that new dishes be prepared and used exclusively for this work. All Vycor dishes must be cleaned by the follow-

Table 9.IV. Comparison of Methods for Cobalt in Petroleum

	Cobalt Concentration (ng/g)			
	Added	*Measured*		
Sample		*Wet Ash HVAA (n = 3)*	*Wet Ash Flame AA (n = 2)*	*Direct HVAA*[a] *(n = 2)*
Crude A	0	1.8	< 2	< 10
Crude B	0	83	108	114
Crude C	0	3.1	4	< 10
	44	46	50	58
Crude D	0	516	495	504
No. 6 residual fuel	0	240	272	258

[a] Diluted with 1:1 xylene-quinoline.

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ing procedure before use. Add 50 ml of 1:1 HCl and boil for 10 min. Discard the HCl solution and take three successive 5-ml portions of concentrated sulfuric acid to fumes in the dish. Wash the dish with water and air dry.

(4) *Air bath.* Cut a cylinder of aluminum, with a diameter slightly larger than that of the dish, to a 2.25 cm length.

(5) *Infrared Lamp,* 250-watt, supported about 0.6 cm above the air bath.

(6) *A variable transformer* to regulate the heat of the infrared lamp.

(7) *Muffle furnace,* capable of maintaining 500° ± 25°C and equipped with a supplementary air or oxygen supply.

(8) *Syringes.* 1-, 5-, 10-, and 100-μl with Teflon tips.

(9) *Volumetric flasks,* 5- and 10-ml.

Reagents. Unless otherwise indicated, reagents are ACS reagent grade. Water is deionized.

(1) *Sulfuric acid,* concentrated.

(2) *Dilute hydrochloric acid.* Add 50 ml of concentrated acid to 950 ml of water.

(3) *Standards*

(a) Stock standards/aqueous cobalt solution, 1000 ppm (Fisher Scientific, etc.)

(b) Calibration standard, 10 μg/ml. Prepare 50 ml of the calibration standard by careful successive dilutions, starting with the 1000 ppm standard. This calibration standard must be prepared immediately before use.

Procedure

(1) *Instrument operation.*

(a) Set up the AA spectrometer and carbon rod atomizer to measure cobalt. Use the following settings as a guide in optimizing the instrument and carbon rod atomizer.

Wavelength, nm	240.7
Lamp current, mA	7.5
Slit, μm	25
Inert gas	Argon
flow rate, l/min	3
pressure, psi	15
Injection frequency, sec	90

CRA-63 Program

		Supply Setting	*sec*
dry (initial)		3	10
dry (final)		20	10
ash		6.5	15
atomize		8	4
Typical response (absorbance/ng)	0.38		

(2) *Sample Decomposition*

(a) Carry a reagent blank through the procedure, starting with 5 ml of sulfuric acid.

(b) Weigh 1–10 g of sample into a Vycor dish. Add 5 ml of concentrated sulfuric acid, mix with a glass stirring rod, and place the dish in an air bath. Place the bath on a hot plate and suspend an infrared lamp above the dish so that the face of the bulb is 2.5 to 5 cm above its top. For light matrices such as gasoline, most of the sample should first be evaporated with a stream of nitrogen before the dish is placed in the air bath.

(c) Heat the sample with the lamp and then with low heat from the hot plate. Stir frequently with a glass rod to break up any surface crust and reduce spattering. Increase the heat gradually until fumes of sulfuric acid are no longer evolved, transfer the dish to the muffle furnace at 500°C, turn on the air or oxygen supply, and ash the residue.

(d) Cool, wash down the walls of the dish with 5 ml of dilute hydrochloric acid, cover, and dissolve the ash by warming on the steam bath. Transfer the solution quantitatively to a 10-ml volumetric flask, dilute to volume with dilute hydrochloric acid, and mix thoroughly.

(e) Transfer accurately a 2-ml aliquot of the digestate (ignore any precipitate) to a 5-ml flask and dilute to volume.

(3) *Measurement of Cobalt*

(a) Insert a new tube furnace between the support rods, and set up to measure cobalt with the recorder set at 5 mv full scale. Clean the atomization furnace by "baking" at maximum temperature several times until an acceptable blank is obtained.

(b) Set the dry, ash, and atomize conditions to the appropriate settings.

(c) Withdraw a 5-μl aliquot of a diluted digestate.

(d) Initiate the atomization program and immediately inject the sample aliquot. After 10 sec from program initiation, increase the "dry" cycle voltage control to its maximum and allow the program to run to completion. Reset the "dry" cycle voltage to its original setting.

(e) Record the peak height caused by absorbance observed during the atomization step of the program.

(f) From the peak heights obtained, select an aliquot of digestate such that the peak height is 10–20 divisions above the blank and background signal. Also select an aliquot of calibration standard such that the peak height (after the third addition) will be about four times the peak height for the original digestate. Use these same aliquots throughout the determination of that sample.

(g) Withdraw the selected aliquot of digestate into a microliter syringe and follow Steps d and e. Repeat three times. If the signals are within ± 10% of their average, continue Step h. Otherwise, repeat Steps d and e twice more and average the five readings.

(h) Add the selected aliquot of working standard solution to the digestate and mix well. Carry out Step g.

(i) Add another aliquot of the working standard to the solution from Step h and repeat Step g.

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(j) Add a third aliquot of the working standard to the solution from Step i and again repeat Step g.

Calculation

(1) Calculate the amount of each standard addition in nanograms (C_i).

(2) Calculate average peak height in chart division obtained from the digestate (A_0) and digestate plus standard additions (A_i).

(3) Subtract the peak height obtained on the blank solution (b) from the average.

(4) For each of the additions calculate

$$\text{ng Co/g} = \frac{(A_o - b)(C_i)(i)}{W(A_i - A_o)}$$

where

A_0 = initial peak height for sample
b = average peak height for blank
i = number of the addition (1, 2, or 3)
A_i = peak height after the i^{th} addition
C_i = amount of cobalt added to the sample in nanograms after i^{th} addition
W = weight of sample

(5) Average the three calculated results and report the final average.

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10

Lead

The ability to determine nanogram quantities of lead in various matrices is important from a number of environmental and health-related aspects. However, the accurate determination of lead at the ng/g level in petroleum and petroleum derived products presents a formidable challenge. The analysis is adversely affected by the ubiquitous presence of lead as a contaminant, an effect that is compounded by the extensive sample preparation necessary to convert the petroleum matrix into a form amenable to analysis by a sufficiently sensitive instrumental technique, such as atomic absorption spectroscopy or differential pulse anodic stripping voltammetry (DPAS).

Available Analytical Methods

Although innumerable papers have been published describing the determination of lead in various matrices, only a limited amount of information is available concerning the analysis for lead at part-per-billion levels in petroleum matrices. Milner (*1*) has reviewed those methods which were directed specifically towards lead in petroleum products at the parts-per-million and -billion levels.

The widespread popularity of atomic absorption spectroscopy utilizing both flame and non-flame atomization sources has resulted in a number of publications describing its use in determining ultratrace levels of lead. Hodkova and Holle (*2*) described the determination of lead in gasoline down to concentrations of 10 ppb after destruction of the alkyl lead with bromine and extraction of the lead with nitric acid. Steinke (*3*) determined lead on an aqueous extract of gasoline at lead levels greater than 10 ppb. Kashiki et al. (*4*) determined lead in gasoline to 1 ppb by atomic absorption spectroscopy with a carbon rod analyzer. Bratzel and Chakrabarti (*5*) also used a carbon rod analyzer in conjunction with an organic-to-aqueous solvent extraction procedure. A detection limit of 2×10^{-12} g (absolute) was obtained using the 283.3-nm lead line. The determination of volatile lead alkyls in gasoline to 1 ppb was reported by Mutsaars and Van Steen (*6*) using a combination of gas chromatography and flame photometry.

These methods which, for the most part, rely on the use of solvent extraction for matrix isolation can be somewhat limited in their applicability. Aqueous extraction procedures can be advantageously applied to

In Analysis of Petroleum for Trace Metals; Hofstader, R., el al.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1976.

light samples such as gasoline, which contains lead as an alkyl lead compound. However, the general applicability of the technique has not been demonstrated on a wide variety of petroleum products, particularly crude oils or more viscous samples, which may either contain unknown forms of naturally occurring lead or are too viscous to manipulate easily. The possibility of incomplete extraction is also present.

Flameless atomic absorption spectroscopy can detect ≤ 50 ng/g lead in gasoline and light distillates, but the low ashing temperatures necessary to prevent preatomization losses make it difficult to separate the lead signal from the background continuum absorption with heavier matrices. Differential pulse anodic stripping voltammetry, which is capable of selectively detecting lead at sub-nanogram levels, has not been extensively applied to petroleum samples because of the inorganic solution requirements of most electrode systems.

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Special Analytical Considerations

Since direct methods of analysis for nanogram/gram levels of lead are limited in applicability, some sample preparation is required to include most petroleum matrices and applicable techniques. A suitable sample preparation procedure is, however, subject to stringent requirements, especially one which can provide a final analyte solution amenable to analysis by electroanalytical techniques.

Techniques such as heated vaporization atomic absorption (HVAA) and differential pulse anodic stripping voltammetry (DPAS) have reduced the absolute sample size requirements to the point where gram or subgram samples can provide sufficient amounts of lead to yield nanogram/gram sensitivity. Smaller sample sizes also provide advantages in that smaller quantities of reagents are consumed. Reduction of sample size, however, amplifies the effects of contamination. The presence of lead as an environmental contaminant complicates this problem.

Wet digestion procedures which involve large acid/sample ratios can contribute excessive amounts of lead contamination. Further addition of reagents aggravates this situation. Since lead is a common impurity in many reagents, especially acids, such reagents must be very carefully purified before use. Also, since lead can be present in the sample either as a volatile organolead compound, inorganic lead, or a mixture of the two, the preparation must ensure that both types of compounds are retained.

Sample Preparation

The importance of lead and the stringent sample preparation requirements prompted the study of several decomposition techniques. Particular emphasis was placed on those techniques which would provide a final analyte amenable to analysis by either DPAS or HVAA. Wet digestion techniques involving the use of "liquid fire," a mixture of H_2SO_4, HNO_3, and $HClO_4$ (*7*), effectively destroy the petroleum matrix. The large acid/sample ratios and resultant strong acid medium, however, require extremely pure reagents and further treatment before quantitation by DPAS.

Efforts to use an in situ micro sulfated ash procedure by ashing the sample with H_2SO_4 directly in a carbon cup atomizer before HVAA atomization (HVAA) were made during this Project. "Creeping" of the sample into the optical path of the spectrometer caused an excessive background absorbance which prevented effective utilization of the technique. Furthermore, recovery studies suggested that the use of H_2SO_4 as an in situ ashing aid caused low lead recoveries. Five nanograms of lead (as $PbSO_4$) were quantitatively recovered after heating for up to 4 hr at 530°C in a muffle furnace. However, the response for lead "ashed" in a HVAA graphite furnace at 600°C with varying amounts of H_2SO_4 was consistently less than those ashed in the furnace at lower temperatures. Therefore, it is postulated that reaction of the lead with the carbon at the higher temperature results in lead losses and that H_2SO_4 increases the effect.

Gorsuch (*8*) performed extensive recovery studies using radiochemical techniques to determine the effect of several ashing variables on lead recoveries from samples of cocoa and dried milk. Lead-212 at either the 1- or 10-ppm level, was quantitatively recovered when HNO_3 was used as an ashing aid at 550°C; recoveries of lead using H_2SO_4 were slightly lower. At 450°C both acids yielded quantitative results.

Nitric acid has been used for digestion prior to lead measurement. The acid, which can be prepared readily in a high degree of purity by sub-boiling distillation, circumvents the problems associated with H_2SO_4 or $HClO_4$.

Kotz et al. (*9*) decomposed biological materials with HNO_3 under pressure in a Teflon tube enclosed in a stainless steel jacket provided with facilities for heating and cooling. A maximum temperature of 170°C was allowed, beyond which the Teflon began to soften. Digestions performed with HNO_3 under pressure reduce the volume of acid required (*10*).

Commercially available pressure decomposition vessels consist of an inner Teflon chamber contained in a stainless steel outer jacket (*11, 12*) or are constructed entirely of Teflon (*13*). All Teflon is more restrictive with respect to temperature and pressure, but is not subject to metallic contamination.

A sample preparation scheme has been developed by the Project which combines the advantageous features of commonly applied tech-

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niques, requires minimal amounts of reagents and decreased manipulative effort, yet is capable of providing a final analyte solution suitable for determining lead at the nanogram/gram level by DPAS. The analyte solution should also be amenable to analysis by HVAA, but this possibility was not explored experimentally. The method involves the wet digestion of the petroleum sample in a Vycor cell with fuming HNO_3 under pressure in an enclosed, commercially available chamber constructed entirely of Teflon, and ignition of the carbonaceous residue in a silica muffle furnace. The ashed residue is dissolved in a minimum amount of concentrated hydrochloric acid, which is then neutralized with anhydrous ammonia vapor. The salt is heated to remove excess ammonia and water, dissolved in a measured amount of water, and subjected to differential pulse anodic stripping voltammetry. This sample preparation procedure offers some significant advantages:

(1) The entire analysis, from digestion to measurement, is performed in a small, easily fabricated, clean Vycor vessel which also serves as an electrochemical cell, thereby eliminating transfer losses and reducing adsorptive losses to a minimum.

(2) The sample contacts only Vycor and during the digestion resides in an enclosed Teflon chamber which serves as a portable mini clean room.

(3) The ashing step is performed in a silica oven containing integrally molded heating elements, further minimizing the risk of contamination.

(4) All reagents used can be readily produced in a very high state of purity and are easily removed by low temperature evaporation.

(5) Performing the digestion in a sealed Teflon chamber ensures that any volatile organolead compounds are retained and permits use of minimum amounts of HNO_3.

(6) The Teflon chambers are inexpensive enough so that a number of digestions can be performed simultaneously. Six vessels can be handled conveniently, thus allowing for replicate analyses and an acceptable sample throughput. Six samples can be processed in from 3 to 4 hr.

(7) The final analyte solution is only mildly acidic, thereby contributing to increased Hg film stability.

Measurement

The fuming HNO_3 digestion procedure was used in conjunction with differential pulse anodic stripping voltammetry to determine sensitivity, linearity of response, measurement precision, and lead background or blank levels. Recovery studies, as well as some interference studies, were also conducted. It should be emphasized that the data presented in this discussion were obtained in a particular laboratory situation. Practical detection limits were determined both by the laboratory environment and by the ability of the analyst to reduce both the variability and magni-

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tude of the analytical blank through strict adherence to experimental detail.

To determine the feasibility of using the method of standard additions for quantitation, the linearity of response was determined. A 250-μl sample of HCl was neutralized with NH_3 and diluted with 2.5 ml of water. Lead stripping curves were obtained for a series of standard additions of 10 μl of 1 ng Pb/μl standard, duplicate stripping curves were obtained for each standard addition, and a detection limit of 10 ng was attained using the given experimental parameters. Precision and linearity were

Table 10.I. Lead Reagent Blank and Total Lead Background Levels

1. *Reagent blank level*

1 ml HNO_3 (evaporated at 140°C) + 250 μl HCl + NH_3

Cell No.	*ng Pb Measured*
1	5.8
2	4.5
3	4.5
4	4.5
5	4.0
9	4.0
	Avg 4.6 ($\theta = 0.66$)

2. *Repeat of above experiment, next day*

Cell No.	*ng Pb Measured*
1	4.4
2	3.3
3	3.5
4	4.3
5	3.7
	Avg 3.8 ($\theta = 0.49$)

3. *Total lead background level*

1 ml HNO_3 (taken through entire digestion procedure)
+ 250 μl HCl + NH_3 + 2.5 ml H_2O

Cell No.	*ng Pb Measured*
1	5.5
2	2.5
7	4.5
8	5.5
9	2.0
	Avg 4.0 ($\theta = 1.7$)

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excellent over the entire 10–120 ng concentration range studied. Stability of the electrode system was demonstrated by the linearity of the calibration curve and the fact that the 26 separate anodic stripping curves were generated over a 2-hr period.

The magnitude and the variability of the lead blank or background level were determined to indicate the precision and the practical lower limit of detection. In these experiments an attempt was made to differentiate between the "reagent blank lead" level and the "total blank lead" level resulting from the entire sample preparation procedure. The results of these experiments are shown in Table 10.I. The results obtained from Experiments 1 and 2 give an indication of the reagent blank levels. The results obtained in Experiment 3 represent the total lead contribution from each of the reagents plus any contribution from the atmosphere and the Vycor cells. No significant statistical difference between the three experiments was observed. Lead blank levels were consistently maintained below 5 ng, with the greatest standard deviation being 1.7 ng. To demonstrate that these values indicated the actual lead present rather than inability of the procedure to recover lead, recovery studies using both inorganic and organic lead standards were done. The results are in Table 10.II.

In the first experiment aqueous lead standards and 0.4 g kerosene were taken through the entire procedure. The recoveries obtained indicate that lead is retained during sample preparation.

In another experiment, Conostan base oil, diluted 1 to 100 with kerosene, was spiked with Conostan D-20 (*14*). These standards with 0.4 g kerosene were taken through the entire procedure. Although recoveries for the 20 ng samples were acceptable, those obtained for the 40 ng samples were low. In further experiments, however, it was demonstrated that incomplete dissolution was responsible for the low recoveries, and essentially quantitative recoveries were obtained when the cells were thoroughly contacted with the acid.

Recommended Method

The closed-system, fuming HNO_3 digestion is capable of fixing nanogram quantities of lead so that it is not lost during the ensuing ashing. The HCl, NH_3 vapor and H_2O treatment quantitatively recovers lead at the nanogram level in the ashed residue if strict adherence to the experimental procedure is maintained, and it can provide a final analyte solution amenable to analysis by differential pulse anodic stripping voltammetry. The DPAS procedure detects nanogram levels of lead with good accuracy and precision. Hg film electrode stability in the NH_4Cl supporting electrolyte solution is satisfactory. Although extensive interference studies have not been performed, recovery studies with D-20 standards indicate that the 20 elements in the mix, at least at the levels present, do not interfere. Cross-check data using this method were not obtained.

Detailed Procedure

Scope. This method describes the determination of lead at the nanogram level in petroleum and petroleum products by differential pulse anodic stripping voltammetry. Practical lower limits of detection are determined by the magnitude and variability of the analytical blank.

Table 10.II. Recovery of Lead by Proposed Method

(All Results in ng Pb/g)

1. Aqueous Pb standards + 0.4 g kerosene

Added	*Measured*[a]	*Added*	*Measured*
20	21	50	52
20	16	50	40
40	37	100	92
40	38	100	95

2. Conostan D-20 Standards + 0.4 g kerosene

Added	*Measured*	*Added*	*Measured*
20	18	50	45
20	17	50	42
40	28	100	70
40	24	100	60

3. Repeat of above experiment, more careful HCl wash

Added	*Measured*	*Added*	*Measured*
40	38	100	95
40	36	100	90

[a] All results were corrected for a 5-ng lead blank level.

Summary of Method. The sample is digested with fuming HNO_3 in an enclosed Teflon chamber. After removal of the carbonaceous matter in a muffle furnace, the residue is dissolved in HCl, which is then neutralized with anhydrous ammonia. The resultant salt is dried, dissolved in a measured quantity of water, and subjected to analysis by anodic stripping voltammetry. Quantitation is achieved by the method of standard additions.

Apparatus

(1) *Electroanalysis instrumentation*

(a) Princeton Applied Research Corp., model-174 polarographic analyzer or eqiuvalent.

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(b) Hewlett-Packard model-7004B X–Y recorder or equivalent.

(2) *Electroanalysis cell and electrode assembly* (Figure 10.1)

(a) Hg-plated, wax-impregnated graphite working electrode (Princeton Applied Research Corp. No. 9319).

(b) A saturated calomel reference electrode (Beckman No. 39178).

(c) A platinum wire counter electrode.

(d) A quartz N_2 de-aeration tube, all held in a swivel-mounted TFE cell cap.

(e) Digestion/electromechanical cells fabricated from Vycor.

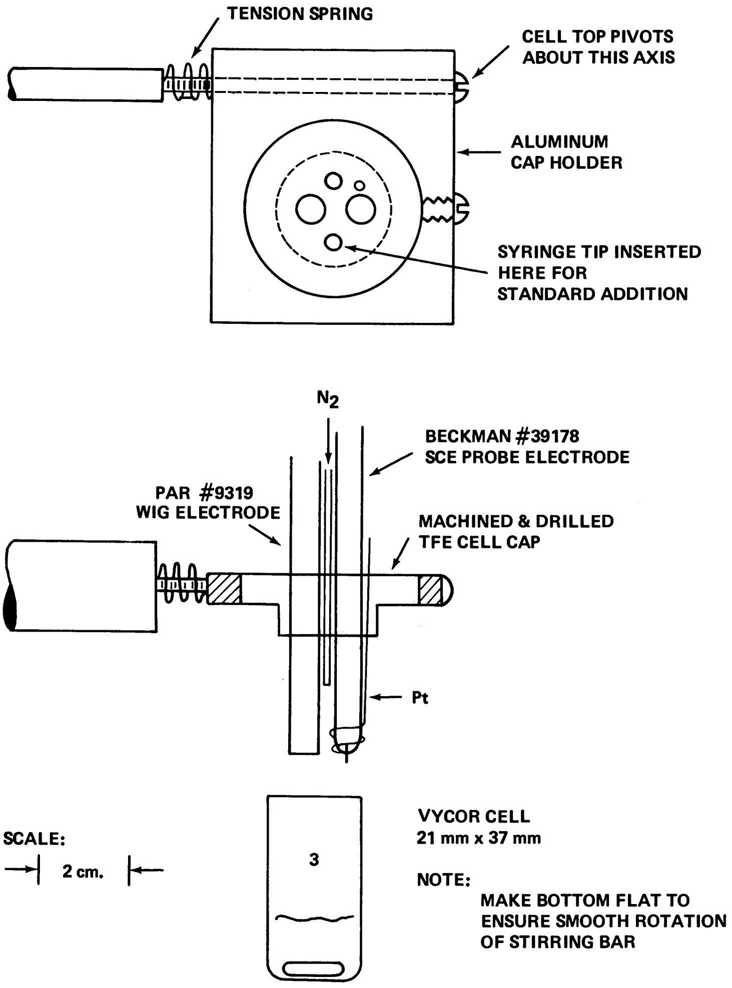

Figure 10.1. Cell and electrode assembly

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(3) *Magnetic stirrer* (No. 14-511-2 Fisher Scientific or equivalent) and TFE coated stirring bars (17 × 3 mm).

(4) *Muffle furnace,* silica lined, containing integrally molded heating elements and capable of maintaining a temperature of 525°C (model 51828 Moldatherm Furnace, Lindberg).

(5) *Hot plate,* capable of maintaining a temperature of 105°C (Temp Blok module heater).

(6) *Syringe,* variable capacity microliter syringe with disposable glass tips.

(7) *H_2O dispenser,* Lab Industries repipet.

(8) *TFE decomposition vessel,* all-Teflon decomposition vessel capable of being sealed and heated to 150°C (Teflon Lorran decomposition vessel (*13*)).

(9) *NH_3 vapor neutralization apparatus* (*Figure 10.2*), a side-arm gas scrubbing tube and vented Teflon cap are connected to the sample cell and an anhydrous NH_3 tank with a needle valve for fine-flow adjustment.

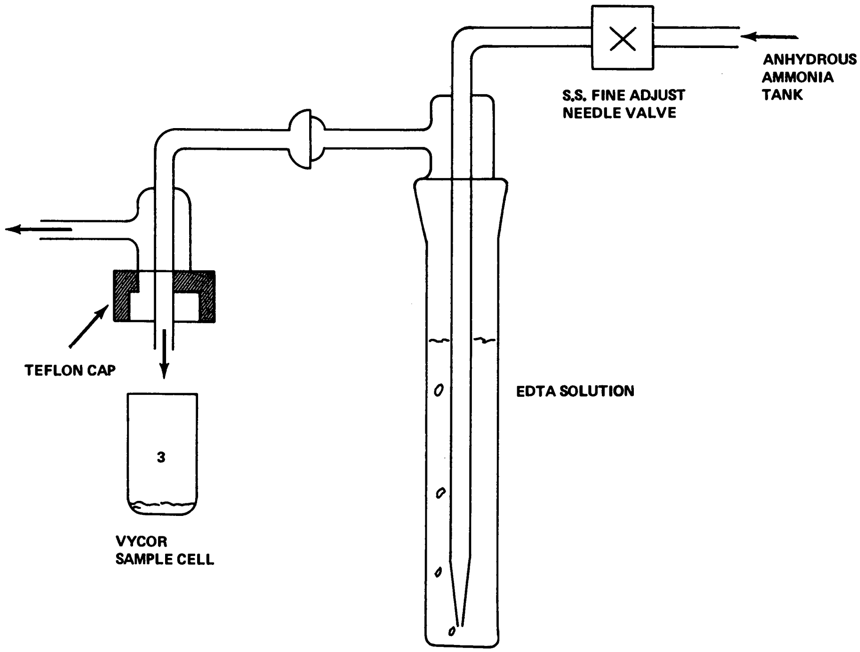

Figure 10.2. Apparatus for NH_3 vapor neutralization of HCl

Reagents and Materials

(1) *Water, ultrahigh purity.* Pass distilled water through organic anion–cation exchange resins (Barnstead demineralizer), double distill from a quartz still (pure water generator, Quartz Products Corp.), and store in a high pressure process polyethylene container; carry out subboiling distillation in a quartz still just prior to use.

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(2) *Fuming nitric acid, high purity.* Purify nitric acid, 90% (J. T. Baker) by sub-boiling distillation from a Teflon still prior to use.

(3) *Nitrogen purge gas, low oxygen.* Pass prepurified nitrogen through hot copper wool (450°C) and humidify by bubbling through high purity water.

(4) *Hydrochloric acid, ultrahigh purity.* Subject hydrochloric acid (Ultrex, J. T. Baker) to sub-boiling distillation in a quartz still.

(5) *Ammonia vapor, high purity.* Purify anhydrous ammonia (Matheson) by bubbling through an EDTA solution.

(6) *Lead standard.*

(a) Stock solution 10,000 ng/μl. Dissolve 1.000 g lead metal (Fisher, certified ACS granular) with 2 ml nitric acid in 10 ml of water and dilute to 100 ml with water.

(b) Calibration lead standard, 1 ng/μl. Dilute stock solution 1 to 100 and further dilute this solution 1 to 100. Prepare this solution just prior to use.

(7) *Mercury plating solution.* Dissolve triple-distilled mercury (0.2 g) with 0.2 ml nitric acid and dilute to 100 ml with water.

Procedure

(1) Optimize instrumental parameters using the following settings as a guide.

Operating mode	differential pulse
Initial potential	— 0.7 V vs. SCE
Range	1.5 V
Rate	10 mv/sec.
Direction	+
Modulation amplitude	25 mv
Output offset	as required
Display direction	+
Low pass filter	off
Current range	as required, typically 0.1 ma
Deposition time	4½ min with stirring 30 sec without stirring

(2) *Sample Preparation.* A reagent blank must be carried through the procedure along with the sample.

(a) Clean the Vycor cells by soaking in 1:1 reagent grade HNO_3, then thoroughly rinse, place on a disposable laboratory tissue, and allow to dry by evaporation.

The following steps, up to placement of the sealed vessels in the furnace, were carried out in an HEPA filtered clean laboratory. Individual laboratory circumstances will determine whether such precautions are possible or even necessary.

(b) Accurately weigh a maximum of 400 mg sample into a cell. Use cleaned disposable dropping pipets to dispense samples. Use Teflon forceps at all times to handle cells and keep them covered as much as possible with inverted crystallizing dishes. It is convenient to process six samples at a time. Perform at least duplicate determinations per sample.

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(c) Place each cell in a Lorran decomposition vessel and add 1 ml of fuming HNO_3. Add the vessel cap and hand tighten. Stainless steel hose clamps should be placed around the caps before use. They minimize leakage of HNO_3 vapor caused by softening of the Teflon during heating.

(d) Tighten the hose clamp with a screwdriver and place the sealed vessels in the furnace at 140°C for 1 hr. A temperature of 140°C is near the lower control limit of the furnace, and the following procedure should be used. The furnace is first equilibrated at 140°C. Use a thermocouple-pyrometer to monitor temperature. In introducing sample vessels first turn OFF furnace power switch before opening the door. Do not turn ON again until the vessels are placed in the furnace, the door has been closed, and a few moments have elapsed. This allows the heat-sensing element to re-equilibrate with the actual furnace temperature. If this is not done, the very fast heating action will result in considerable thermal overshoot. Depending on the physical condition of the vessels and the tightness of the seal, some nitric acid fumes may escape from the vessels during the digestion. This is not serious unless copious fumes indicate a very poor seal.

(e) Remove the vessels from the furnace, allow to cool for ½ hr, then loosen the clamps and remove the caps. *CAUTION*: Wear plastic gloves and open in a hood.

(f) Remove the cells from the vessels with Teflon forceps, place the cells in the furnace, and raise the furnace temperature to 525°C to remove the carbonaceous matter.

(g) Remove the cells from the furnace, allow to cool; add 250 μl concentrated HCl to each cell, rotate the cells so as to wash the entire interior, and allow to stand for 1 hr.

(h) Place the cell containing the dissolved residue in position in the neutralization apparatus shown in Figure 10.2 and flow a gentle stream of ammonia vapor over the solution. The gentle boiling and refluxing action caused by the heat of reaction serves to further ensure complete dissolution of the residue. Continue this process for at least 7 min or until excess ammonia is present. A slushy, white residue will result.

(i) Heat each cell for 30 min at 105°C, keeping it covered with an inverted crystallizing dish that minimizes atmospheric contamination.

(j) Dissolve the residue in 2.5 ml H_2O dispensed from a volumetric dispenser and add a magnetic stirring bar to the cell.

(3) *Preparation of Hg film electrode.* The Hg film electrode, although possessing superior sensitivity characteristics, is more subject to irreproducible behavior than is the hanging Hg drop electrode. The following plating procedure is satisfactory.

(a) Place a cell containing Hg plating solution in position, deaerate the solution for 3 min with N_2 and apply a potential of — 0.45 V vs. SCE for 10 min without stirring.

(b) Remove the cell, rinse the electrode assembly copiously with H_2O, and remove H_2O droplets by application of a laboratory tissue. *Do not touch the Hg coating.*

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(c) Position the electrodes in a blank electrolyte solution and obtain a stripping curve by scanning from — 0.7 to — 0.2 V vs. SCE. Maintain the potential at — 0.2 V for about 1 min to ensure complete cleaning of the electrode. Monitor the performance of the Hg film electrode by observing the response to the addition of a standard. Symmetrical peaks of uniform height should result. If response begins to change drastically, or if unsymmetrical or double peaks begin to appear, wipe the electrode clean and replate. In "real" samples other elements may be present which are plated either reversibly or irreversibly along with the lead to affect the quantitative stripping of the lead from the film. It is therefore desirable to "clean" the electrode after each run by holding a potential of — 0.2 V, while stirring, for about a minute after each stripping curve is obtained and to monitor its response constantly.

(4) *Quantitation of lead*

(a) Place a cell containing the dissolved residue in position, push the N_2 inlet capillary into the solution and deaerate for 3 min.

(b) Leave the N_2 flowing and raise the tube out of, but slightly above, the solution and turn ON the magnetic stirrer.

(c) Apply a potential of — 0.7 V vs. SCE for 4½ min, turn OFF the magnetic stirrer, and wait 30 secs.

(d) Sweep the potential from — 0.7 to — 0.2 V. Turn the stirrer ON and hold the potential at —0.2 V for 1 min.

(c) Obtain replicate stripping curves to establish measurement precision.

(f) Add a suitable standard solution by inserting the syringe containing the standard through a hole in the cell top beneath the surface of the sample solution while stirring. While, for maximum accuracy, the concentration of the standard should depend on the initial concentration, a sequential addition of two 10-μl aliquots of a 1 ng/μl standard has been found suitable for the 0–100 ng range. It is important that the standard be added in this manner. Removing the cell from the electrode assembly, adding the standard solution, and replacing the cell in position results in irreproducible results.

(g) Remove the cell and rinse the electrodes with H_2O after completion of the standard additions steps. Do not forget to push down the N_2 inlet capillary and rinse it since it has contacted the sample solution. If the amount of lead present is greater than 100 ng, run a blank solution through the stripping procedure to ensure cleanliness of the electrode system.

Calculation

(1) Measure the lead peak height in scale units on the anodic stripping curve obtained for the sample solution.

(2) Measure the peak heights recorded after each of the standard additions.

(3) Plot the three peak heights against the total nanograms Pb added after each addition and extrapolate to the baseline; record the total nanograms determined in the solution.

(4) Repeat Steps 6.1–6.3 for the reagent blank.

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(5) Calculate the concentration of lead in the sample as follows:

$$\text{ng Pb/g sample} = \frac{\text{ng Pb in sample solution} - \text{ng Pb in blank solution}}{\text{sample weight}}$$

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11

Manganese

The origin of manganese in various petroleum matrices is not well understood. Traces of it in crude oil may arise as oil-soluble components native to the oil reservoir, as entrained brine, or as corrosion products from equipment used in production. The fate of this manganese in the refinery is likewise unclear. Although it may be concentrated in distillation processes, it has also been deposited on spent cracking catalysts. In addition to "native" forms, part-per-million levels of manganese may be introduced into petroleum matrices as an additive to improve fuel oil combustion or as an antiknock additive to gasoline.

Available Analytical Methods

Generally, the manganese reported in petroleum has been measured as part of trace-element survey analyses by neutron activation (*1, 2, 3*) or by emission spectroscopy (*4*). Prior to the work of the Trace Metals Project no procedure was available specifically for the determination of traces of manganese in petroleum. Manganese levels above 1 μg/ml have been determined colorimetrically after oxidation to permanganate with periodate (*5*). Concentrations as low as 0.001 μg/ml have been measured by the catalytic effect of manganese on the oxidation of diethylamine by periodate (*6*). In both methods, however, chromium must be eliminated before measurement. After removal of nickel and iron, manganese has been measured polarographically down to 0.2 μg/ml (*7*). Pulse polarography has extended the detection limit to $\geq$ 0.03 μg Mn/ml (*8*). Flame atomic absorption has a sensitivity of 0.024 μg/ml when applied directly to aqueous media (*9*). This sensitivity has been extended to less than 0.01 μg/ml by solvent extraction with cupferron and MIBK (*10*). Heated vaporization atomic absorption (HVAA) has been used at the μg/ml level in aqueous media (*11, 12, 13, 14*). In addition, HVAA has been used directly to determine manganese in petroleum matrices at the part-per-million level (*15*). The Trace Metals Project has extended the use of direct HVAA to allow the determination of manganese down to 10 ng/g in a variety of petroleum matrices. The work has been described in detail; in general, it involves the use of standard additions to a solution of the sample in tetrahydrofuran (*16*).

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Role of Neutron Activation

Manganese can be readily determined in petroleum matrices by INAA. The principal radiation at 847 keV [(^{55}Mn ($n\gamma$) ^{56}Mn)] can be used to detect less than 10 ng/g after 1-hr irradiation at a neutron flux of 10^{12} cm^{2-} sec^{-1}. Counting times are only 10–30 min. The presence of large amounts of iron may cause interference from the ^{55}Fe (n,p) ^{56}Mn daughter produced fission neutrons in the reactor. To correct for this interference, the intensity ratio of the 1099 KeV ^{59}Fe/847 Kev ^{56}Mn is determined by simultaneous irradiation of a pure iron solution. The magnitude of the interference is calculated from the 1099 KeV ^{59}Fe peak intensity in the sample. This technique was applied in the Project to validate the HVAA procedure which was developed.

Special Analytical Considerations

In the development of the procedure, the effect of several HVAA operating parameters (of a Varian Techtron CRA-63 atomizer) were investigated (*16*). The ashing temperature and composition of the "sheathing" gas affected the atomization peak height at high ashing temperatures, causing some losses of manganese. This is consistent with reported losses of manganese when dry ashing is carried out above 700°C (*17*). The introduction of hydrogen into the sheathing gas reduces the atomization peak height even when the "normal" ashing temperature was used. The mechanism that reduces the signal is unclear.

Once atomization conditions had been optimized, "native" manganese could be successfully analyzed directly in petroleum samples by HVAA. Since a fixed amount of manganese as the sulfonate (Conostan) or the cyclohexanebutyrate (NBS) gave identical peak heights, the manganese signal appears to be independent of its compound form. To demonstrate quantitative retention, the direct technique was applied to several matrices, and the results were compared with those obtained by alternate techniques. Some representative data for manganese are given in Table 11.I, where the direct HVAA results are compared with those obtained

Table 11.I. Comparison of Direct HVAA Procedure with Results Obtained after Ashing

	Manganese Concentration (ng/g)		
Sample	*Direct HVAA*	*Ash-Aqueous HVAA*	*Ash-Flame*
No. 6 fuel oil	306	283	300
Crude oil E	104	112	—
Heating oil	32.5	39.0	—
Crude oil F	42.4	38.0	—

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by HVAA and flame AA after ashing. In the latter cases the sample was charred with sulfuric acid, ignited at 450°C for 2 hr, and the residue taken up in aqueous acid. The agreement between the two methods indicates that "native" manganese was not lost prior to the atomization in the direct procedure.

Whenever the direct technique is applied to known compounds, the validity must be established. For example, the additive methylcyclopentadienyl manganese tricarbonyl may be too stable to be analyzed by direct HVAA without pre-atomization losses. Some work has suggested that losses of this compound occur even in acid digestion procedures (*4*). No studies were made on this compound as part of the Project.

Sample Preparation

In the direct HVAA procedure a 2.5-g sample is diluted to 5 ml with tetrahydrofuran. Further dilutions are made in the same solvent when the initial solution concentration is too high.

Measurement

The atomization conditions for the CRA-63 were optimized empirically to give a range of 0–50 μg/ml with 1-μl injections of dilute standards (*16*). Under these conditions the linearity covered 0–400 ng/ml, and the calculated detection limit ($S/N = 2$) was 0.5 pg. Background corrections, where necessary, were made using the 280.2-nm lead line. A HGA-70 atomizer was used in one of the cooperating laboratories after a similar empirical optimization.

When the absorbances for addition of a known quantity of a manganese standard to several matrices were compared, substantial differences were observed (Table 11.II). If the direct HVAA technnique were independent of matrix effects, all the numbers would be identical to the 1.80 value in THF alone. However, the matrix effects equilibrated after a single injection, and they were retained after the sample had been analyzed. This "matrix memory" was eliminated by multiple atomizations at maximum power between samples. Although this behavior is similar to that for Cr or V (*see* Chapters 8 and 14), no relationship has been established between the Mn response and the levels of Fe, Ni, or V in these matrices (*16*). Consequently, the method of standard additions is recommended to compensate for these effects.

Recommended Method

In the procedure, a 2.5-g sample is diluted with tetrahydrofuran, injected into the HVAA atomization tube, and the heating program is

Table 11.II. Effect of Matrix on the Determination of Manganese by Direct HVAA Procedure

Sample	*Change in Absorbance (× 1000)/ppb Mn Added*
THF	1.80
Crude A	1.82
Crude B	0.88
Crude C	1.93
Crude D	1.75
Crude E	1.23

started. The sample concentration is determined from the background-corrected sample signal by standard additions using a computation which has been described (*16*).

The data in Table 11.I demonstrate that the combination of standard additions and background correction successfully overcomes matrix effects to give accurate results. Similar excellent agreement has been obtained between HVAA and neutron activation data, as discussed below.

The precision of the procedure was established at the initiating laboratory in a variety of matrices. Some representative data, presented in Figure 11.1, indicate a 17% relative standard deviation for the procedure.

Six samples were prepared for a cross-check program. The resuts obtained at four participating laboratories are shown in Figure 11.2. For comparison the values obtained by neutron activation are indicated by

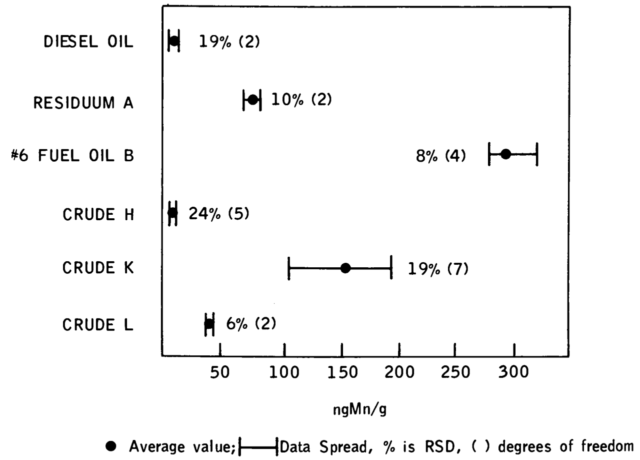

Figure 11.1. Intralaboratory data for determination of manganese

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the triangles. The relative standard deviation at any one site was approximately 10% on the No. 2 heating oil and the Ellenberger crude and 30% on the Light Arabian crude. This includes one laboratory where the data were obtained with a Perkin-Elmer HGA-70 after the operating parameters were adapted. When the precision between laboratories was calculated, with statistical elimination of some data, the relative standard deviations were 20% for the No. 2 heating oil and Ellenberger crude and 26% for the Light Arabian crude.

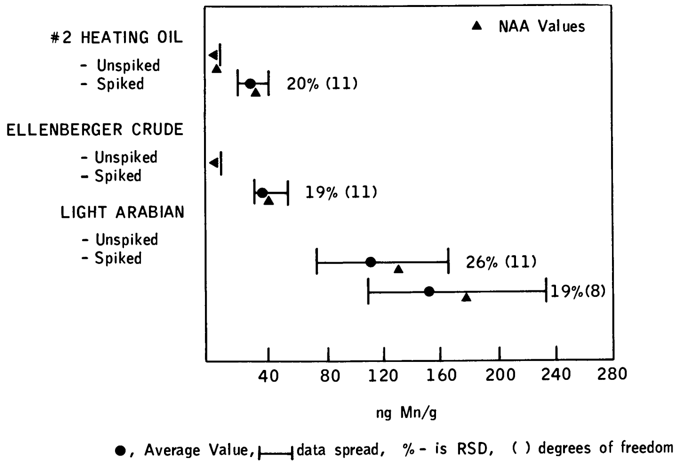

Figure 11.2. Interlaboratory data for determination of manganese

Detailed Procedure

Scope. The method is designed to determine manganese concentrations down to the 10 ng/g level in petroleum and petroleum products.

After setup, each sample requires about 30 minutes for analysis. However, sample preparation and apparatus setup limit output generally to 12 samples in one day.

Summary of Method. The sample is diluted with tetrahydrofuran, and the metal in the solution is measured with an atomic absorption spectrophotometer equipped with a carbon rod atomizer (CRA-63). The concentration of metal is calculated on the basis of changes in the absorption resulting from standard additions to the sample solution.

Apparatus

(1) *Carbon rod atomizer,* Varian Techtron model 63 or equivalent.

(a) 9-mm Pyrolytically coated atomization furnaces tubes (Varian-Techtron).

(b) FX-9I support electrodes (Poco Graphite).

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(2) *Atomic absorption spectrophotometer* (*AAS*), Jarrell-Ash 82-532 or equivalent.

(a) Strip chart recorder, 0–10 mv with 0.5-sec response time (Leeds & Northrup Speedomax W or equivalent).

(b) Manganese hollow cathode lamp (Jarrell Ash or equivalent).

(c) Lead hollow cathode lamp (Jarrell Ash or equivalent).

(3) *Syringe,* with Teflon tip or Teflon needle, capable of delivering 1-μl samples reproducibly.

(4) *Micropipettes,* 5-, 10-, and 50-μl (capillaries, syringe, or Eppendorf pipettor).

Reagents

(1) *Tetrahydrofuran* (THF) ACS reagent grade.

(2) *Standards*

(a) Conostan, Mn standard, 5000 ppm (w/w) manganese in oil (Continental Oil Co.).

(b) Stock 1000-μg/ml standards. Weigh 2 g Conostan 5000-ppm (w/w) standard into a 10-ml volumetric flask and dilute to volume with THF.

(c) Calibration standard (5 μg/ml). Dilute 50 μl of 100-μg/ml stock standard to 10 ml with THF.

Procedure. Initially all glassware must be cleaned with (1:1) nitric acid prior to use. The equipment is then rinsed several times with THF.

(1) Weigh 2.5 g oil sample into a 5-ml volumetric flask and dilute to volume with the solvent.

(2) Optimize the HVAA for manganese with the tube furnace in the optics using the following settings as a guide.

Wavelength (nm)	279.4
Inert gas-(l/min)/psi	N_2 4/10
Furnace	9-mm tube
Aliquot used	1 μl
CRA-63 program	(V/sec)
dry	2/20
ash	6.5/30
atomize	8/3

When the operating parameters are optimized, scale expansion should be used so that each 25 ng Mn in 5 ml solvent gives between 10 and 20 scale units. If samples contain > 5× detection limit levels of Mn, a further dilution of the sample should be made before standard additions. This dilution technique is recommended rather than changing operating parameters. The residual heat in the atomization tube contributes to the repeatability of sample signals. This effect may be minimized by injecting samples on a fixed schedule. For the method described here, injections made at 90-sec intervals give good repeatability.

(3) Aliquot 1 μl of the sample solution into the syringe, initiate the CRA-63 program, and inject the sample aliquot immediately.

(4) Record the peak height caused by absorbance observed during the atomization step of the program.

(5) Repeat Steps 3 and 4 two more times; calculate the average. If the three signals are within ± 10% of the average, use this value in the final calculation; if not, repeat the sequence Steps 3 and 4 two more times and use the average of the five readings.

(6) Record the average reading of the sample solution as A_0.

(7) Add 5 μl of the calibration standard (equivalent to 25 ng) to the same solution, mix well and carry out Steps 3–5. Record the average peak height as A_1.

(8) Add a second 5 μl of the calibration standard (25 ng, a total of 50 ng) to the sample solution and again carry out Steps 3–5. Record the average peak height as A_2.

(9) Add a third 5 μl of the calibration standard (25 ng, a total of 75 ng) to the sample solution and again carry out Steps 3–5. Record the average peak height as A_3.

(10) Reset wavelength to 280.2 nm and inject the sample solution (Step 9) to measure background. Record the reading as b.

Calculation

(1) Calculate the concentration of manganese in the sample from the first addition (Step 7) as:

$$\text{ng Mn/g} = \frac{(25\ \text{ng Mn})}{A_1 - A_0} \times \frac{A_0 - b}{2.5\ \text{g}}$$

(2) Repeat the calculation for the second addition:

$$\text{ng Mn/g} = \frac{(50\ \text{ng Mn})}{A_2 - A_0} \times \frac{A_0 - b}{2.5\ \text{g}}$$

(3) Repeat the calculation for the third addition:

$$\text{ng Mn/g} = \frac{(75\ \text{ng Mn})}{A_3 - A_0} \times \frac{A_0}{2.5\ \text{g}}$$

(4) Average the three values (Steps 1–3) and report that number as ng Mn/g in the sample.

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12

Mercury

The determination of mercury in petroleum and petroleum products has become increasingly important, as its association with fossil fuels has been more broadly recognized. However, a method which can be readily implemented using generally available laboratory equipment has been needed for accurate measurement to the low ng/g level in these matrices.

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Available Analytical Techniques

Except neutron activation, methods which have been used to determine mercury in organic materials involve a matrix decomposition step prior to the actual measurement. Oxidative techniques involving various combinations of acids and salts have been widely used for matrix destruction (*1, 2, 3, 4, 5*), as have the Schöniger, Wickbold, and other bomb and tube combustion techniques (*1, 6, 7, 8, 9, 10*).

Various measurement techniques have been used after matrix destruction. Small amounts of mercury are generally determined by conversion from an ionic species in aqueous solution to the elemental vapor, which is measured spectroscopically by atomic fluorescence, ultraviolet, or atomic absorption techniques (*1, 5, 6, 9, 10, 11, 12, 13, 14, 15, 16*). Review articles covering the determination of small amounts of mercury in organic and inorganic samples (*17*) and the determination of mercury by nonflame atomic absorption and fluorescence spectroscopy (*18*) have recently appeared. In certain instances detection limits of 1 ng/g have been possible.

Role of Neutron Activation

Neutron activation has been used to study mercury levels in some crude oils (*19*). The choice of isotope used for measurement depends on the interfering elements in the samples. With [^{196}Hg (n,γ) ^{197}Hg, 77 KeV, $T_{1/2}$ = 65 hr], a 10 ng/g detection limit is readily achieved with 1-hr irradiation at a neutron flux of 10^{12} n cm^{-2} sec^{-1}. However, inherent sulfur or chloride (from entrained formation water) create serious interferences in some crudes. The fission neutrons (fast) from these elements produce ^{32}P ($T_{1/2}$ = 14 days) and ^{35}S ($T_{1/2}$ = 87 days), both of which contribute

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Advances in Chemistry; American Chemical Society: Washington, DC, 1976.

significant Bremsstrahlung radiation in the 77-KeV region. To avoid this, the ^{203}Hg isotope is often used. This isotope [^{202}Hg (n,γ) ^{203}Hg, 279 KeV, $T_{1/2} = 46.9$ days] requires several hours irradiation time to reach the 10-ng/g level. In this case, a major interference is caused by overlap by the 279 KeV gamma from ^{75}Se. Correction for this interference can be made by simultaneous irradiation of a selenium standard solution to determine the 265/279 KeV intensity ratio for ^{75}Se. This ratio and the measured peak intensity of the 265 KeV ^{75}Se in the sample are then used to correct for the interference in the ^{203}Hg region.

Neutron activation analysis of mercury in petroleum should always be carried out in quartz vials in place of the conventional snap-cap polyethylene vials. As noted in the section on Storage and Stability, the latter frequently lead to serious mercury losses after irradiation (*see* Chapter 2).

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Special Analytical Considerations

It has been reported that inorganic mercury is lost from acidified aqueous solutions (*20, 21*) and that elemental mercury can be lost by diffusion through the walls of polyethylene containers (*22*). During the Project's study, 100-ng/g solutions of mercury (as diphenylmercury) in oils were stable for at least 3.5 months in containers of polypropylene, Teflon, soft glass, and Pyrex glass (*23*). The stability of "real" samples to be analyzed for mercury is uncertain since the native mercury compounds in petroleum are unknown.

Care must be taken to avoid contamination from the time the sample is collected until the measurement is made. Elemental mercury is often present in the laboratory atmosphere as a result of the use of manometers or polarographs and the breakage of thermometers. Contamination of samples stored in polyethylene bottles has been reported to occur by diffusion of elementary mercury contained in the ambient air into the bottles (*24*).

Large and variable amounts of mercury have been found in various laboratory reagents which might be used during mercury determination (*25*). Therefore, the mercury content of reagents must be determined before they are used.

Sample Preparation

The Project investigated two methods for sample decomposition before mercury measurement. One involved acidic oxidation, and the other involved combustion in a Wickbold oxy-hydrogen burner (*26*).

Acid Digestion. The digestion apparatus (Figure 12.1) is a modification of that reported to retain quantitatively μg quantities of mercury during the acid decomposition of cocoa (*27*). A separate addition funnel

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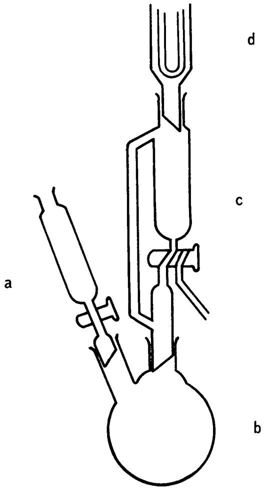

Figure 12.1 Apparatus for wet oxidative decomposition of oils

(a) was included because two separate doses of nitric acid were required in the decomposition of oils. In use, an oil sample and sulfuric acid are placed in the flask (b), and nitric acid is added. The mixture is refluxed until the oxidative activity of the nitric acid is exhausted, the mixture is heated to fumes of sulfuric acid, and additional nitric acid is added.

Nitric acid washing of glassware, even if not previously used for mercury determinations, often did not remove all traces of mercury. Large, variable mercury contamination can be encountered during determinations, but the contamination appears constant on a given day. To avoid the effects of mercury contamination, a mercury-free oil—e.g., a white oil—must be carried through the procedure until an acceptable mercury blank is obtained.

Wickbold Decomposition. The Wickbold decomposition apparatus is shown schematically in Figure 12.2. It consists of a sample reservoir, stainless steel burner, quartz combustion chamber, and an absorber con-

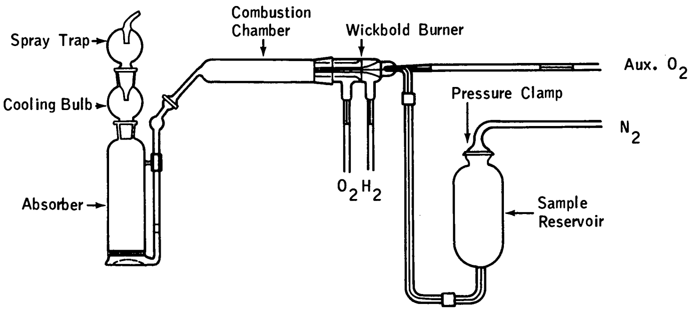

Figure 12.2. Wickbold apparatus

taining an acidic permanganate solution. Pressure regulators for oxygen, nitrogen, and hydrogen are not shown. A sample of oil, diluted with an appropriate solvent, is burned in the oxy-hydrogen flame, and the mercury is collected in the absorber.

Some distillates may be burned without dilution, and low boiling distillates may be diluted with isooctane before burning. However, a benzene–2-propanol diluent is preferred over isooctane for samples of crude oils. The permanganate color must persist in the absorber during the burn, or mercury will be lost. A mercury reagent blank as high as 160 ng was found to be associated with different lots of potassium permanganate.

The use of an oxy-hydrogen burner different from a Wickbold burner produced reducing gases that decolorized the permanganate in the absorber during the early burning stages and therefore rendered the scrubbing solution inactive towards mercury. Optimum fuel/oxidant conditions must be established before a burner is used in conjunction with mercury measurements.

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Measurement

Measurement was by cold-vapor atomic absorption (CVAA), which is based on the reduction of ionic mercury to the elemental form by divalent tin. The resultant elemental mercury is swept by a gas stream through a quartz-windowed absorption cell which is placed in the beam of a mercury lamp of an atomic absorption spectrometer. Hatch and Ott (*11*) optimized this measurement system in their study of the mercury content of geological samples. Since their work, this method of mercury measurement has gained widespread popularity because of its sensitivity and relative simplicity. Two recent reviews which cover the Hatch and Ott technique and its subsequent modifications have appeared (*17, 18*).

The detection limit for mercury varies according to the design of the cold-vapor apparatus. Some workers have reported a detection limit of 1 ng of mercury (*28*). In cases where the method is used in conjunction with the determination of mercury in organic matrices, the lower useful limit of the technique has been found to be 1–10 ng of mercury per gram of sample (*17, 18*).

Interferences which were encountered include broad-band absorption at the 253.7-nm mercury line caused by residual organic matter in the sample, fogging of the windows of the absorption cell by water vapor, and oxidizing materials in the sample which prevent the reduction of ionic mercury to elemental mercury by divalent tin. Careful control of the analytical conditions can overcome these interferences.

The Project investigated two cold-vapor systems. The "closed" system, which is illustrated in Figure 12.3, consists of a borosilicate absorp-

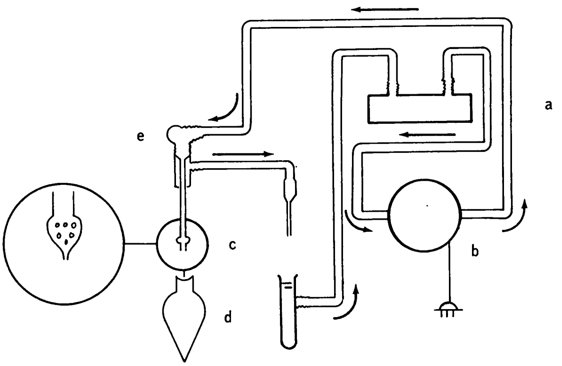

Figure 12.3. Apparatus used for cold-vapor mercury absorption measurement

tion cell with quartz windows (a), oscillating plastic-lined pump (b), a variable transformer (not shown), bubbler (c), a pear-shaped flask (d), and a water knock-out trap (e), all connected with Tygon tubing. This system can be modified into a "flow through" system by omitting the pump, opening one end of the cell to the atmosphere, and connecting the other to a compressed air supply. Both systems performed satisfactorily.

Application to Acidic Digestates. Acidic digestates are extracted with hexane to remove organic matter that might absorb at the 253.7-nm mercury measurement line. The digestates are then treated with hydroxylamine sulfate to destroy any strong oxidizing materials which prevent reduction of ionic mercury to elemental mercury.

The mercury reagent blank for the nitric acid cannot be measured by generating elemental mercury from a solution of 1:3 nitric acid with divalent tin. However, it can be determined by adding potassium permanganate and sulfuric acid, heating the solution to remove the nitric acid, and measuring the mercury after treatment with hydroxylamine sulfate.

Application to Acidic Permanganate Absorber. In the Wickbold apparatus the mercury is collected in the acidic permanganate absorber. In this case, a solution of hydroxylamine must be added to the absorber prior to measurement to reduce all the manganese to the divalent state, in which form it does not interfere with the reduction of ionic mercury to elementary mercury by tin(II).

Recommended Methods

Acid Digestion—Cold-Vapor Atomic Absorption Method. The sample and concentrated sulfuric acid are combined in a reflux digestor. The mixture is treated with several portions of concentrated nitric acid

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and brought to sulfuric acid fumes until most of the organic matter is destroyed. The digestate is then extracted with hexane, treated with an acidic hydroxylamine solution, and the mercury is measured by cold-vapor atomic absorption.

Evaluation of the accuracy of the method was complicated because no certified oils of low-level mercury content were available, because the types of mercury compounds which might occur in petroleum were unknown, and because the recovery of mercury might depend upon oil composition. However, a recovery study was carried out by adding organomercury compounds to unspiked oils which had been shown to contain < 10 ng Hg/g. Some of the results were obtained for samples which had been spiked with coal, certified to contain 127 ng Hg/g by the U.S. National Bureau of Standards. While mercury might not be present in petroleum in the same form as it is in coal, the results indicate that

Table 12.I. Recovery of Mercury by Proposed Procedure

	Mercury Concentration (ng/g)		
Oil	*Added*	*Measured*	*Hg Added as*
Crude oil A	50	46, 55	diphenylmercury
	25	32, 32, 14	diphenylmercury
	15	12	diphenylmercury
Fuel oil	40	32	mercury octanoate
White oil	25	17, 21, 22	mercury in coal (NBS SRM 1630)
	13	9, 11, 15	mercury in coal (NBS SRM 1630)

Table 12.II. Recovery of Mercury by Proposed Method

	Mercury Concentration (ng/g)		
	Run 1	*Run 2*	*Run 3*
Diesel fuel	< 10[a]	< 10	< 10
Diesel fuel + 42 ng Hg/g	38	37	44
Net	38	37	44
No. 2 heating oil	< 10	< 10	< 10
No. 2 heating oil + 42 ng Hg/g	35	37	44
Net	35	37	44
Crude A	< 10	< 10	< 10
Crude A + 42 ng Hg/g	34	36	33
Net	34	36	33

[a] All < 10 values assumed to be 0. Average net Hg = 38 ± 3 ng/g.

Table 12.III. **Recovery of Mercury by Wickbold Combustion Method**

Sample	*Mercury Concentration (ng/g)* *Added*	 *Measured*
Isooctane	none	< 5
Crude oil A	none	< 5
Crude oil B	23	23
Crude oil C	1020	920
Crude oil D	1030	1090

mercury associated with a fossil fuěl is recovered using this procedure. The data in Table 12.I indicate that at concentrations between 15 and 50 ng Hg/g, the procedure will give results within approximately 20% of the true value.

The data in Table 12.II were obtained from the analysis of base oils and oils spiked to contain 42 ng Hg/g. The mercury content of the base oils was < 10 ng/g, and that of the spiked oils was 38 ng/g. The standard deviation was 3 ng/g.

Wickbold Decomposition—Cold-Vapor Atomic Absorption Method. The oil sample is dissolved in benzene:2-propanol, and introduced into the flame by pressuring with nitrogen. The combustion gases are trapped in an absorption solution containing potassium permanganate, sulfuric acid, and nitric acid in the absorber. The mercury content is measured by the "flow-through" CVAA technique. The data in Table 12.III show that by this procedure mercury was quantitatively recovered from a Hg-free crude oil to which diphenylmercury was added (crude oil A).

Three crude oil samples, spiked with diphenylmercury to contain 20, 44, and 99 ng Hg/g, were analyzed by two different laboratories. Although one laboratory appears to have a high bias (Table 12.IV), the intralaboratory standard deviation is 4 ng/g, and the interlaboratory standard deviation is 11 ng/g. The results obtained by either method agree satisfactorily with those obtained by INAA (Table 12.V). Consequently, either procedure will provide values that are within 20% of the true value at the 20- to 100-ng/g level.

Table 12.IV. **Recovery of Mercury by Wickbold Combustion—Cold-Vapor Atomic Absorption Method**[a, b]

Sample	*Hg Added*	*Mercury Concentration (ng/g)* *Initiating Laboratory*	 *Cooperating Laboratory*
Crude C	20	21	36
Crude B	49	48	72
Crude A	99	86	143

[a] Overall intralaboratory standard deviation = 4 ng/g.
[b] Overall interlaboratory standard deviation = 11 ng/g.

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Table 12.V. Mercury Content of Oils: Comparison of Methods

	Mercury Concentration (ng/g)[a]			
Sample	*Added*	*INAA*	*Wet Oxidation CVAA*	*Wickbold—CVAA*
Diesel fuel	0	10	10	6, 7
	42	54	40	42
No. 2 heating oil	20	60	35	36
Crude C	49	27	28	21
Crude B	42	59	55	48
Crude A	99	44	34	38
		121	—	86

[a] Average data from two to six determinations.

Detailed Procedures

The acid decomposition procedure was developed using a recirculating cold-vapor atomic absorption technique for measurement. The Wickbold decomposition procedure used a flow-through cold-vapor atomic absorption measurement technique. Consequently, each measurement technique is presented with the decomposition procedure used in its development. However, since the two measurement techniques are comparable, either may be used after the alternate decomposition technique.

Wickbold Combustion—Cold-Vapor Atomic Absorption Method

Scope. This method is applicable to the determination of mercury in petroleum and petroleum products (except leaded gasoline) which can be burned in a Wickbold apparatus. The method is capable of measuring the amount of mercury in a sample down to the 5-ng/g level. The upper limit of the method as presented is determined by the linearity of the mercury calibration curve (Figure 1.2). Three to four samples can be analyzed conveniently at one time, and the average analysis time is about 2 hr.

Outline of Method. A sample is weighed into a beaker, dissolved in benzene:2-propanol, and burned in an oxy-hydrogen flame using a Wickbold combustion apparatus. The combustion products are collected in a 5% sulfuric–nitric acid mixture containing potassium permanganate. Prior to measurement, trapped mercuric salts are reduced to elemental mercury with tin(II) chloride. The mercury is then swept out of solution and measured by cold-vapor atomic absorption spectroscopy.

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Apparatus

(1) *Wickbold combustion apparatus* (*Figure 12.2*). This consists of a 250-ml sample reservoir, stainless steel burner, quartz combustion chamber, gas pressure regulators for oxygen, nitrogen, and hydrogen, and an absorber fitted with an extra-coarse frit (Koehler Instrument Co.).

(2) *Mercury atomic absorption and generation system*

(a) Atomic absorption cell. A borosilicate glass cylinder, 2.5 cm in diameter and 10 cm long, with two side arms, and with quartz windows held at each end with epoxy cement.

(b) Anhydrone drying trap. A short piece of glass tubing (5 cm) filled with Anhydrone held in place with glass wool.

(c) Compressed air

(d) Stopcock with $ joint to match inlet of Wickbold absorber.

(e) Tygon tubing

(3) *Atomic absorption spectrophotometer.* Any instrument able to accommodate a 10 cm absorption cell is suitable. A Perkin-Elmer model 403 instrument was used in developing this method.

(4) *Mercury hollow cathode lamp*

Reagents

(1) *Nitric acid,* concentrated (high purity). Unless otherwise indicated, reagents are ACS reagent grade. Water is deionized.

(2) *Sulfuric acid,* concentrated

(3) *Hydrochloric acid,* concentrated

(4) *Potassium permanganate*

(5) *Hydroxylamine hydrochloride solution,* 12%. Dissolve 12 g of hydroxylamine hydrochloride in water and dilute to 100 ml.

(6) *Absorbing solution.* Dissolve 2 g of potassium permanganate in 90 ml of water; add 5 ml each of concentrated nitric and sulfuric acids.

(7) *Tin(II) chloride solution,* 10% in 20% HCl. Dissolve 10 g of tin(II) chloride dihydrate in 20 ml of hot, concentrated hydrochloric acid. When the hot solution becomes clear, dilute to 100 ml with water.

(8) *Benzene*

(9) *2-Propanol*

(10) *Mercury standard*

(a) Stock standard, 1.00 mg/ml. Dissolve 0.1354 g of mercury (II) chloride in 100 ml of 0.3*M* sulfuric acid.

(b) Calibration mercury standard, 0.1 μg/ml. Pipet 1.00 ml of the stock mercury solution into a 100-ml volumetric flask and dilute to volume with water. Pipet 1.00 ml of the diluted solution into another 100-ml volumetric flask and dilute to volume with water.

(11) *Blank solution,* 50 ml of 4:1 benzene:2-propanol.

Instrument Parameters

(1) Optimize the atomic absorption spectrometer instrument for the determination of mercury. The following parameters, which apply to the Perkin-Elmer model 403 AA instrument, may be used as a guide.

Analytical wavelength	253.7 nm
Damping	average of 10 counts
Mercury lamp current	ma
Digital concentration readout	absorbance mode
Aspiration rate	1 liter of air/min

Mercury Atomic Absorption Cell Assembly

(1) Connect the compressed air to the on-off stopcock; establish flow rate of 1 liter/min, and turn the stopcock OFF.

(2) Assemble the system components in the following sequence using Tygon tubing connections: stopcock, Wickbold absorber, drying trap, and absorption cell.

(3) Attach the absorption cell to 10-cm burner with rubber bands and optically align the cell to give minimum absorbance of the 253.7-nm line.

(4) Place an absorber containing 200 ml of water in the generation train and open the stopcock. Zero the absorbance while flushing air through the system.

Calibration

(1) Add 1, 2, 5, 10, and 20-ml portions of the mercury calibration standard to a series of Wickbold absorber vessels, each containing 100 ml of the absorbing solution. The solutions will contain 0.1, 0.2, 0.5, 1.0, and 2.0 μg of mercury. At the same time start a blank.

(2) Add, dropwise, sufficient hydroxylamine hydrochloride solution to reduce the potassium permanganate (usually 10–20 ml).

(3) Connect the outlet of the absorber to the inlet of the atomic absorption cell. Add 10 ml of tin(II) chloride solution, and immediately connect the air supply to the inlet of the absorber. The mercury will be flushed out of the solution.

(4) Note the gradual increase in absorbance and record the maximum.

(5) Continue flushing until the absorbance is again zero. The elemental mercury should be vented to an appropriately scrubbed hood.

(6) Plot a calibration graph of absorbance vs. μg of mercury over the range of 0–2 μg.

Sample Preparation Procedure

(1) Weigh 20 g of oil into a 250-ml beaker and add 40 ml of benzene and 10 ml of 2-propanol. Dissolve the sample completely, then transfer the oil solution quantitatively into the sample reservoir of the Wickbold apparatus. This procedure is for samples estimated to contain 5–150 ng/g of mercury. Smaller samples can be taken if higher amounts of mercury are present.

(2) Adjust the oxygen regulator on the Wickbold apparatus to 9 psi and the hydrogen regulator to 3 psi. Immediately light the burner with the induction coil and attach the combustion chamber to the burner.

(3) Add the absorbing solution to the absorber, attach the spray trap, and attach to the outlet of the combustion chamber. Increase the

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nitrogen pressure on the sample reservoir carefully until the flame is several inches long (nitrogen pressure ~ 4 psi).

(4) Burn the entire sample (normally 1.5 hr); shut off the nitrogen. Rinse the reservoir with two 5-ml washings of benzene.

(5) Shut down the Wickbold apparatus by turning off the nitrogen, hydrogen, and oxygen in this order. Remove the absorber. Wash the spray trap and the cool combustion chamber with a stream of water into the absorber.

(6) Measure the mercury concentration in the absorber solutions of the blank (*see* Reagents, Item 11) and the samples by the procedure given in the Calibration section, starting at Item 2.

Calculation

(1) Convert the absorbance to micrograms of mercury from the calibration curve and calculate the mercury content of the sample:

$$\text{Mercury, ng/g} = \frac{(N - B)\ 1000}{W}$$

where:

N = micrograms of mercury in sample

B = micrograms of mercury in blank

W = sample weight, grams

Acid Digestion Procedure

Scope. This method is applicable to the determination of mercury in petroleum and petroleum products in amounts greater than 10 ng/g. Three samples can be analyzed in an 8-hr working day.

Outline of the Method. The sample is digested in a mixture of concentrated sulfuric and nitric acids in an apparatus which ensures that volatile mercury compounds are not lost during the oxidation of the oil. After the digestion is complete, the digestate is diluted with water and then extracted with hexane to remove water-insoluble unreacted organic matter. Residual traces of hexane are then removed by sweeping nitrogen through the extracted solution. The digestate is then treated with hydroxylamine sulfate solution, and the mercury content is measured by cold-vapor atomic absorption spectroscopy.

Apparatus

(1) *Digestion apparatus* (*Figure 12.1*).

(a) Funnel, separatory, cylindrical (d), 60-ml \$ 24/40, Teflon stopcock.

(b) Distilling receiver (c), \$ 24/40, Teflon stoppered, available from Lab Glass, No. LG-6400T, modified with a 12.5 mm od medium wall side arm.

(c) Two-necked flask (b), vertical type, 500 ml, \$ 24/40.

(d) Friedrich condenser (d), \$ 24/40, 325 mm.

(e) Heating mantle, 500 ml.

(f) Variable transformer, 0-120 volts.

(g) Magnetic stirrer

(h) Teflon-coated magnetic stirring bar

(i) Separatory funnel, 500 ml, Teflon stopcock.

(2) *Apparatus for generating mercury vapor (Figure 12.3).*

(a) Flask, pear-shaped, single necked, 300 ml, $\overline{\$}$ 14/35, available from Kontes, No. 608700.

(b) Bubbler, $\overline{\$}$ 14/20.

(c) Test tube, 16 mm × 100 mm, $\overline{\$}$ 14/20, filled with glass wool.

(d) Impinger, $\overline{\$}$ 14/20, compatible with test tube.

(e) Pump, oscillating, Gorman-Rupp No. 11968, available from Macalaster-Bicknell Co.

(f) Absorption cell, quartz windows, 20 cm length × 22 mm diameter, equipped with hose fittings.

(g) Tygon tubing

(3) *Atomic absorption equipment*

(a) Atomic absorption spectrophotometer, Perkin-Elmer 403 or equivalent.

(b) Hollow cathode mercury lamp

Reagents

(1) *Concentrated sulfuric acid,* suitable for mercury determination, J. T. Baker, No. 9685.

(2) *Concentrated nitric acid,* suitable for mercury determination, J. T. Baker, No. 9603.

(3) n-*Hexane,* Burdick and Jackson.

(4) *Hydroxylamine solution,* 12 g hydroxylamine sulfate, 12 g hydroxylamine sulfate, 12 g sodium chloride, and 100 ml of deionized water.

(5) *Tin(II) sulfate solution,* 10% tin(II) sulfate in 0.2*N* sulfuric acid.

(6) *1000 mg/ml mercury stock solution,* 1.354 g mercury(II) chloride diluted to 1 liter with 1*N* sulfuric acid.

(7) *Potassium permanganate solution,* 5% potassium permanganate in deionized water.

Acid Digestion of Oil (Refer to Figure 12.1). Thoroughly clean all glassware with 1:1 nitric acid:deionized water, rinse with deionized water, and dry. Once the digestion has been started, the procedure must be carried through the measurement of the mercury on the same day.

(1) Add 5 g of oil, 25 ml of concentrated sulfuric acid, and a magnetic stirring bar to the two-necked flask. Assemble the apparatus as indicated in Figure 12.1 (lubricate the joints with H_2SO_4). Place a heating mantle and a safety shield in front of the apparatus.

(2) Start the magnetic stirrer and add 50 ml of concentrated nitric acid dropwise from the addition funnel. Bring the mixture to reflux over a period of 1.5 hr and then reflux for 1.5 hr.

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(3) Bring the mixture to fumes of sulfuric acid by collecting the volatiles in the distillation receiver. Allow the mixture to fume 5 min after all the volatiles have been collected.

(4) Cautiously add 25 ml of concentrated nitric acid dropwise from the addition funnel. Continue to collect the volatiles during this addition, then bring to fumes of sulfuric acid as in Step 3 and allow the mixture to fume 5 min.

(5) Return the entire contents of the distillation receiver to the flask dropwise (**CAUTION**). Allow the mixture to reflux for 15 min.

(6) Close the stopcock and collect the volatiles in distillation receiver. Bring the mixture to fumes of sulfuric acid and allow to fume 5 min.

(7) Repeat Step 5, then allow the mixture to cool to room temperature.

(8) Wash the interior of the condenser and distillation receiver into the flask, using approximately 100 ml of deionized water. Do not allow the temperature of the flask to exceed 35°C. To avoid a large temperature rise resulting from the addition of water to the acid mixture, place the flask in an ice bath and add the water in small increments.

(9) Transfer the contents of the flask quantitatively to the separatory funnel. Extract the mixture with three 100-ml portions of *n*-hexane. Discard the hexane extracts.

(10) Bubble nitrogen through the extracted digestate until the residual traces of hexane are removed. Do not allow nitrogen to bubble through the digestate for an extended time after the hexane has evaporated.

(11) Stir the digestate and add 20 ml of the hydroxylamine solution dropwise.

(12) Continue stirring the solution until the evolution of gas is complete and then sweep out the air space above the liquid with nitrogen.

(13) Adjust the volume of the solution to the 250 ml with deionized water.

(14) Measure the absorbance (A_1) of the solution as indicated in Step 1 under Measurement of the Mercury (below).

Mercury Content of the Reagents

(1) *Reagent blank*

(a) Evaporate a solution consisting of 150 ml of deionized water, 5 ml of the potassium permanganate solution, 25 ml of concentrated sulfuric acid, and 75 ml concentrated nitric acid on a hot plate until fumes of sulfuric acid are reached.

(b) Allow the solution to cool to room temperature, add 100 ml of deionized water, keeping the temperature below 35°C (**CAUTION**), and extract the solution three times with 100-ml portions of *n*--hexane.

(c) Discard the hexane extracts. Bubble nitrogen through the extracted aqueous solution until the residual traces of hexane are removed, but do not allow the nitrogen to bubble through the digestate for an extended time after the hexane has evaporated.

(d) Stir the aqueous solution and add 20 ml of the hydroxylamine solution to the digestate.

(e) Continue stirring the solution until the evolution of gas is complete and then sweep out the air space above the liquid with nitrogen.

(f) Adjust the volume of the solution to 250 ml and measure the absorbance (A_3) of the solution as indicated in Step 1 under Measurement of the Mercury (below).

(2) *Permanganate and hydroxylamine blank*

(a) Measure the absorbance (A_4) of a solution containing 230 ml of deionized water, 5 ml of the potassium permanganate solution, and 20 ml of the hydroxylamine solution as indicated in Step 1 of Measurement of the Mercury (below).

(3) *Hydroxylamine blank*

(a) Measure the absorbance (A_5) of a solution containing 230 ml of deionized water and 20 ml of the hydroxylamine solution as indicated in Step 1 of Measurement of the Mercury (below).

Measurement of the Mercury

(1) *Calibration*

(a) Turn on the atomic absorption instrument. Allow the instrument to stabilize and optimize measuring for mercury. The conditions for the 403 given in the following table serve as a guide.

Slit	5
Range	UV
Wavelength	253.7 nm
Source	use recommended operating current given on the lamp
Lamp	mercury hollow cathode
Mode	concentration
Concentration	110.5
Function	10 average, repeat

(b) Position the absorption cell in the center of the beam generated by the hollow cathode mercury vapor lamp and assemble the remaining apparatus shown in Figure 12.3 with the exception of the pear-shaped flask.

(c) Prepare 250 ml of solution containing 100, 200, 300, and 400 ng of mercury in 10% sulfuric acid by suitable dilutions of the 1000 ng/ml mercury stock solution.

(d) Place each solution, in turn, into the pear-shaped flask, add 10 ml of the tin(II) sulfate solution, and rapidly connect the flask to the apparatus.

(e) Auto-zero the atomic absorption instrument and set the variable transformer to ~ 60 V. Record the absorbance (A_1) caused by the elemental mercury after the absorbance reading stabilizes (ca. 5 min).

(f) Turn off the variable transformer, disconnect the tubing from the inlet side of the pump, set the auto transformer to ~ 65 V, and exhaust the elemental mercury in the system to a hood.

(g) After all the mercury has been exhausted (ca. 10 min), set the transformer to 60 V, reconnect the tubing, and record the absorbance reading (A_2) after it stabilizes (ca. 5 min.).

(h) Plot ($A_1 - A_2$) vs. ng Hg to obtain the calibration curve for the system.

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Calculation

(1) *Absorbance of acidic solutions*

(a) Determine the absorbance $Aa = (A_1 - A_2)$ caused by the mercury contained in the digestate of the oil sample (Step 14 under Acid Digestion of Oil).

(b) Determine the absorbance $Ab = (A_3 - A_2)$ caused by the mercury contained in the solution obtained in Step 14 under Mercury Content of the Reagent.

(c) Determine the absorbance $Ac = (A_4 - A_2)$ caused by the mercury contained in the solution obtained in Step 2 under Mercury Content of the Reagent.

(d) Determine the absorbance $Ad = (A_5 - A_2)$ caused by the mercury contained in the solution obtained in Step 3 under Mercury Content of the Reagent.

(2) *Mercury Content of Sample*

(a) Determine the absorbance caused by the mercury contained in the oil sample:

$$A_{\text{oil}} = Aa - Ab + Ac - Ad$$

(b) Determine the nanograms of mercury corresponding to A_{oil} from the calibration curve obtained in Step 1h under Measurement of the Mercury.

(c) Calculate the amount of mercury in the oil sample:

$$\text{ng Hg/g} = \frac{\text{ng Hg}}{\text{g Sample}}$$

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Molybdenum

Molybdenum has been qualitatively detected in crude oils (*1, 2*). However, its distribution has not been extensively studied because a suitable quantitative method for low concentrations has not been available. In addition to naturally occurring molybdenum, minute quantities can be introduced into distillate fuels by exposure to some processing catalysts or by carryover from the crude.

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Available Analytical Methods

Numerous methods for determining macro concentrations of molybdenum are available. Optical emission spectroscopy has been used in survey-type analyses (*2*), but it does not have adequate sensitivity to measure part-per-billion levels. X-ray fluorescence has been applied for part-per-million levels but cannot be readily extended to the lower levels of interest to the Project. Kinetic methods (*3*) and colorimetry with suitable pre-concentration (*4*) are capable of measuring part-per-billion levels of molybdenum but have not been applied to petroleum analysis. Molybdenum has been determined by atomic absorption techniques in such materials as sea water, biological tissue, and soils (*5, 6, 7*). Although a procedure for determining metals including molybdenum in petroleum by atomic absorption has been reported (*8*), no actual data are given for molybdenum. Flame and heated vaporization atomic absorption of aqueous solutions of ashed samples were selected by the Project for concurrent study in two separate laboratories.

Role of Neutron Activation

Part-per-billion levels of molybdenum can be measured by neutron activation. After two or more hours irradiation at a neutron flux of 10^{12} n cm^{-2} sec^{-1}, the principal gamma at 141 KeV [$^{98}\mathrm{Mo}(n,\gamma,\beta)\ ^{99m}\mathrm{Tc}$] is readily measured. In crude oils, however, some Bremsstrahlung interference may be encountered as a result of activated sulfur or chlorine.

Special Analytical Considerations

The destruction of petroleum samples prior to the determination of molybdenum by either dry or wet ashing is straightforward. Relatively

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few difficulties have been reported; however, molybdenum may be lost when the ash is ignited at high temperatures (*9, 10*). This loss is caused by the volatility of molybdenum oxides which are formed during ignition.

Sample Preparation. Two sample preparation procedures were used. In one, the sample was dry ashed, and the molybdenum was determined by flame AA. In the other, the sample was wet ashed with sulfuric acid, and the molybdenum was determined by HVAA. In each case the carbonaceous residue was ignited in a muffle furnace to an inorganic ash which was subsequently dissolved in dilute acid.

The possibility that molybdenum would be lost when the residue was ignited to an inorganic ash was investigated. In one set of experiments, sodium molybdate was placed in a muffle at 520°C for varying times. Although little or no molybdenum was lost during the first hour, about half was lost in 2-4 hr and all was lost in 12 hr. At 480°, none was lost in 3 hr. In a companion experiment, a No. 2 fuel oil spiked with molybdenum sulfonate and a crude oil containing native molybdenum were dry ashed and ignited for 3 hr at various temperatures. Recoveries of molybdenum indicated no loss up to 520°C (Table 13.I). Similar results were obtained on two other crude oils, which were wet ashed with sulfuric acid before being ignited. Although this study indicated that temperatures up to 520°C could be used to destroy carbonaceous material without causing loss of molybdenum, a temperature of 480°C was selected to minimize the possibility of loss through accidental overheating. There

Table 13.I. Loss of Molybdenum Caused by Temperature[a]

Sample	*Temperature, °C*	*Molybdenum Concentration*	
		Added[b]	*Measured*
No. 2 fuel oil	450	1000	1000
	480		1030, 1000
	510		1030, 970
	520		1030, 970
	520	100	100
	590		60
	650		30
	700		20
	760		20
Crude oil	480	None	46
	520		46
	590		40
	650		31
	700		40
	760		30

[a] Time in furnace: 3 hr.
[b] Added as molybdenum sulfonate.

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was no evidence of contamination from extraneous sources of molybdenum during either type of decomposition, nor was there any detectable molybdenum in the reagents used.

Measurement. FLAME ATOMIC ABSORPTION. To obtain sufficient sensitivity for the measurement of molybdenum by flame atomic absorption, it is necessary to use a nitrous oxide–acetylene flame. Optimum conditions were established empirically by using standard aqueous molybdenum solutions. With the instrument used, the response of the flame AA measurement was linear up to a concentration of 100 μg/ml, with a detection limit (S/N = 2) of 0.1 μg/ml. With the ash from an original 100 g of sample and a final solution volume of 10 ml, a detection limit of 5–10 ng Mo/g was obtained.

Even with the high temperature of the nitrous oxide–acetylene flame, interferences are encountered. The ionization of molybdenum, which reduces sensitivity, was overcome by adding 2000 μg/ml potassium to all solutions. Calcium has been reported to interfere with the determination of molybdenum, but the interference can be suppressed to an insignificant level by the addition of aluminum (*11*). Consequently, 500 μg Al/ml was added to each sample and standard.

HEATED VAPORIZATION ABSORPTION. A Varian Techtron CRA-63 was used. The operating parameters were adjusted empirically so that no molybdenum was volatilized prematurely during the ash cycle and so that the maximum absorption was obtained in the atomize cycle. Under optimum conditions, the response was linear from 0 to 5 ng Mo, with a detection limit of 4×10^{-11} g. This corresponds to a level of 8 ng/g in a 10-g sample.

Because of the high power setting necessary to atomize molybdenum, response was often variable. As in the case of vanadium (Chapter 14), the life of the carbon rod was short. Response dropped significantly because the furnace and support rods deteriorated, resulting in loss of electrical contact and therefore lower atomization temperatures. Replacement was necessary after every 20–25 measurements.

Although the oxide is volatile, no loss of molybdenum was detected in the pre-atomization step, which suggest that the reaction with the carbon of the furance to form the carbide is the favored reaction. The formation of refractory molybdenum carbide not only accounts for the retention of molybdenum prior to atomization, but it also explains the extremely high temperature required to achieve atomization.

The effect of several concentrations of a mixture of 14 metals on the molybdenum absorption was studied (Table 13.II). Although insufficient work was done to relate the interference to specific metals, it is apparent that the method is subject to interference when other metals are present in a concentration appreciably higher than that of the molybdenum. That

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is likely to be the case with a number of the elements listed, particularly with crude oils and residual fuels. Consequently, the technique of standard additions was adopted.

High salt concentrations, of the order of 500 μg of other metals per milliliter, produce multiple peaks during the atomization and mask the molybdenum peak. The peaks are most likely caused by scattered light from salt particles. The difficulty is avoided if the sample size and solution volume are selected to provide a maximum of 10 μg/ml of other metals.

Table 13.II. Effect of Other Elements on HVAA Measurement of Molybdenum[a]

Concentration of Each Interfering Metal,[b] *μg/ml*	*Avg. Response, mm*	*Std. Dev. of Absorption, mm*
0	48	6
0.5	48	8
5	39	8
50	15	4

[a] Molybdenum concentration: 0.5 μg/ml.
[b] Solution contained Si, Al, Cr, Cu, Fe, Mg, Na, Mn, Zn, Ca, Pb, V, Ni, Co.

Recommended Methods. Two methods are suitable. In one, a large sample (usually 100 g) is dry ashed in a porcelain crucible. The resulting carbonaceous residue is ignited in a muffle furnace at 480°C. The ash is dissolved in dilute nitric acid, and potassium chloride and aluminum chloride are added to the solution. The molybdenum is measured by atomic absorption in a nitrous oxide–acetylene flame and related to a calibration curve.

Table 13.III. Precision and Recovery by Dry Ash–Flame AA Method[a]

Molybdenum Concentration (ng/g)			
Added	*Measured*	*Std. Dev.*	*Detns.*
25	27	3.5	11
100	99	4.3	10

[a] Sample: No. 2 fuel oil spiked with molybdenum sulfonate.

In the other method, a smaller sample (typically 20 g) is decomposed by heating with concentrated sulfuric acid. The resulting carbonaceous residue is ashed in a muffle furnace at 480°C. The ash is dissolved in dilute hydrochloric acid, and the concentration of molybdenum is measured by HVAA using the method of standard additions.

Recovery of molybdenum by the dry ash–flame AA method was evaluated on a No. 2 fuel oil sample spiked at two levels with molybdenum sulfonate (Table 13.III).

Table 13.IV. Precision and Recovery by Wet Ash–HVAA Method[a]

Sample	*Molybdenum Concentration (ng/g)* *Added*	*Found*	*% Recovery*
Gasoline	0	< 2	—
	24	27	112
	287	282	98
No. 2 heating oil	0	< 2	—
	57	54	95
Crude A	0	22	—
	75	94	96
Crude B	0	10	—
	98	106	98

[a] Standard Deviation: from 10 to 25 ng Mo/g: 4.5 ($n = 7$)
from 60 to 100 ng Mo/g: 10 ($n = 7$)

The wet ash–HVAA method was evaluated by analyzing several crude oils, a heating oil, and a gasoline, all of which had also been spiked with molybdenum sulfonate (Table 13.IV). Quantitative recovery was obtained on all samples, and precision was acceptable. Furthermore, native molybdenum in four crude oils was determined independently in two laboratories, each using one of the methods (Table 13.V). The interchangeability of the two decomposition and two measurement procedures was studied by determining native molybdenum in a No. 6 residual fuel (Table 13.VI).

Table 13.V. Comparison of Methods for Determining Molybdenum in Crude Oil

	Molybdenum Concentration (ng/g) *Laboratory 1: Dry Ash–Flame AA*	*Laboratory 2: Wet Ash–HVAA*
Crude A	19, 15	23, 20
Crude B	12, 12	11, 9
Crude C	10, < 10	17, 16, 12
Crude D	< 10, < 10	7, 9

Table 13.VI. Comparison of Methods for Determining Molybdenum in a No. 6 Residual Fuel

Method	*Measured (ng Mo/g)*	*n*	*Std. Dev., ng/g*
Wet ash–HVAA	90	3	9
Dry ash–HVAA	96	3	2
Wet ash–flame AA	89	3	12
Dry ash–flame AA	89	5	6

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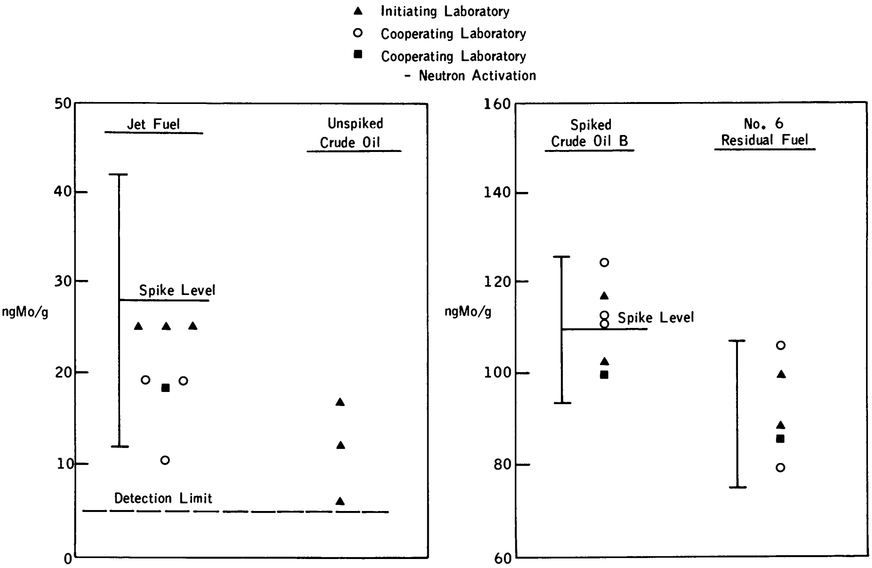

Figure 13.1. Determination of molybdenum in petroleum by different laboratories

Although the ashing and measurement techniques are interchangeable and yield equivalent results, the wet ash–HVAA method is considered preferable for general use because:

(1) The standard additions technique compensates for interferences.

(2) The HVAA measurement is more sensitive, so smaller samples may be used or lower detection limits attained.

On the other hand, the dry ash–flame method is easier, since both the preliminary treatment and the measurement technique are simpler. Where neither of the above conditions exist to make the wet ash–HVAA method attractive, the dry ash–flame method can be used with equal success.

The wet ash–HVAA method was selected for use in the interlaboratory cross-check program because of its greater applicability. A detailed procedure is given at the end of this chapter. For the program, a crude oil, a jet fuel, and a No. 6 residual fuel oil were selected. The crude oil was analyzed in both the native state and after spiking with 110 ng Mo/g. The jet fuel was found to contain no native molybdenum and was spiked with 28 ng/g. The residual fuel was analyzed in its native (unspiked) state only.

The results are shown in Figure 13.1. The vertical lines on the chart represent two standard deviations about the spike level for the jet fuel and crude oil and about the mean of the results for the No. 6 residual fuel. Another cooperating laboratory also determined molybdenum in the

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samples by neutron activation analysis, and these results are also shown in the chart. The cooperating laboratory did not detect molybdenum in the unspiked crude oil either by the wet ash–HVAA method (< 5 ng Mo/g) or by neutron activation (< 10 ng Mo/g), while the initiating laboratory found 12 ± 5 ng Mo/g. At the 95% level of confidence ($\pm 2\sigma$) the two values are not significantly different. The overall within-laboratory standard deviation of the wet ash–HVAA method was ± 8 ng Mo/g over the range 30–110 ng Mo/g. This precision is comparable with that obtained by the initiating laboratory.

Detailed Procedure

Scope. The method is used to determine molybdenum in petroleum and petroleum products at levels down to 10 ng/g. Six to 12 samples can be processed conveniently in a batch, with a total working time of 8 hr.

Summary of Method.

A large sample (up to 100 g) is decomposed by heating with sulfuric acid. The resulting carbonaceous residue is ashed in a muffle furnace at 480°C. The ash is dissolved in dilute hydrochloric acid and diluted to 10 ml. The concentration of each metal is measured on 2-μl aliquots of the digestate by heated-vaporization atomic absorption, using the method of standard additions.

Apparatus

(1) *Atomic absorption spectrometer,* Varian-Techtron AA5 or equivalent.

(a) Strip chart recorder, 0-10 mv with 0.5-sec response time (Leeds & Northrup Speedomax W or equivalent).

(b) Molybdenum hollow cathode lamp, Varian-Techtron or equivalent.

(2) *Carbon rod atomizer,* model 63 (Varian-Techtron).

(a) Pyrolytic-graphite coated atomization furnaces (Varian-Techtron).

(b) Support electrodes, manufactured by Ringsdorff-Werke, GMBH, type RW 0124 (Varian-Techtron).

(3) *Vycor dish.* Cut an 800-ml beaker to a 10-cm height. It is strongly recommended that new dishes be prepared and used exclusively for this work. All Vycor dishes must be cleaned by the following procedure before use. Add 50 ml of 1:1 HCl and boil for 10 min. Discard the HCl solution and take three successive 5-ml portions of concentrated sulfuric acid to fumes in the dish. Finally, wash the dish with water and air dry.

(4) *Air bath.* Cut a cylinder of aluminum with a diameter slightly larger than that of the dish to a 9.5-cm length.

(5) *Infrared lamp,* 250-watt, supported about 2.6 cm above the air bath.

(6) *A variable transformer* to regulate the heat of the infrared lamp.

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(7) *Muffle furnace,* capable of maintaining 480° ± 25°C and equipped with a supplementary air or oxygen supply.

(8) *Syringes,* 1-, 5-, 10-, and 100-μl with Teflon tips.

(9) *Volumetric flasks,* 5- and 10-ml.

Reagents. Unless otherwise indicated, reagents are ACS reagent grade. Water is deionized.

(1) *Sulfuric acid,* concentrated.

(2) *Hydrochloric acid,* dilute. Add 50 ml of concentrated acid to 950 ml of water.

(3) *Standards*

(a) Stock standard 1000 ppm. Aqueous molybdenum standard (Fisher Scientific, etc.).

(b) Calibration standard (20 μg/ml). Prepare 50 ml of the standard by careful successive dilutions, starting with the 1000-ppm standard. This calibration standard must be prepared immediately before use.

Procedure

(1) *Instrument operation*

(a) Set up the AA spectrophotometer and carbon rod atomizer to measure molybdenum. Use the parameters listed in the following table as a guide in optimizing the instrument and carbon rod atomizer.

Operating Conditions

Wavelength, nm	313.3
Lamp current, ma	7.5
Slit, μm	100
Inert gas	Argon
flow rate, l/min	3
pressure, psi	15
Injection frequency, sec	90

CRA-63 Program

	Supply Setting	*Sec*
Dry (initial)	3	10
Dry (final)	20	10
Ash	8	15
Atomize	9.5	6
Typical response (absorbance/ng)	0.18	

(2) *Sample Decomposition*

(a) Carry a reagent blank through the procedure, starting with 5 ml of sulfuric acid.

(b) Depending on concentrations, weigh a 20 to 100 g sample into a Vycor dish. Add 5 ml of concentrated sulfuric acid, mix with a glass stirring rod, and place the dish in an air bath. Place the bath on a hot plate and suspend an infrared lamp above the dish so that the face of the bulb is 2.6–5.2 cm above its top. For light matrices such as gasoline, most of the sample should first be evaporated with a stream of nitrogen before the dish is placed in the air bath.

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(c) Heat the sample with the lamp and then with low heat from the hot plate. Stir frequently with a glass rod to break up any surface crust and reduce spattering. Increase the heat gradually until fumes of sulfuric acid are no longer evolved, transfer to the muffle furnace at 480°C, turn on the air or oxygen supply, and ash the residue.

(d) Cool, wash down the walls of the dish with 5 ml of dilute hydrochloric acid, cover, and dissolve the ash by warming on the steam bath. Transfer the solution quantitatively to a 10-ml volumetric flask, dilute to volume with dilute hydrochloric acid, and mix thoroughly.

(e) Remove a convenient portion (1–2 ml) for standard addition analysis (5.0-ml volumetric flask is a convenient container).

(3) *Measurement of Molybdenum*

(a) Insert a new tube furnace between the support rods and set up to measure molybdenum with the recorder set at 5-mv full scale. Clean the atomization furance by "baking" at maximum temperature several times until an acceptable blank is obtained.

(b) Set the dry, ash, and atomize conditions to the appropriate settings.

(c) Withdraw a 1-μl aliquot of the digestate.

(d) Initiate the atomization program and immediately inject the sample aliquot. After 10 sec from program initiation, increase the dry cycle voltage control to its maximum and allow the program to run to completion. Reset the dry cycle voltage to its original setting.

(e) Record the peak height caused by absorbance during the atomization step of the program.

(f) From the peak heights obtained, select an aliquot of digestate such that the peak height is 10–20 divisions above the blank and background signal. Also select an aliquot of the calibration standard such that the peak height (after the third addition) will be about four times the peak height for the original digestate. Use the same aliquots throughout the determination of that sample.

(g) Withdraw the selected aliquot of digestate into a microliter syringe and follow Steps d and e. Repeat three times. If the three signals are within ± 10% of their average, continue to Step h. Otherwise, repeat Steps d and e twice more.

(h) Add the selected aliquot of working standard solution to the digestate and mix well. Carry out Step g.

(i) Add another aliquot of the working standard to the solution from Step h and repeat Step g.

(j) Add another aliquot of the working standard to the solution from Step i and again repeat Step g.

Calculation

(1) Calculate the concentration of each standard addition in μg/ml.

(2) Tabulate the peak height measurements in chart divisions obtained from the digestate and digestate plus standard additions. Subtract the peak height obtained on the blank solution from the sample peak heights.

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(3) Calculate the best straight line by least squares by the equations:

$$a = \frac{\Sigma Y \Sigma X^2 - \Sigma X \Sigma XY}{M \Sigma X^2 - (\Sigma X)^2}$$

$$b = \frac{M \Sigma XY - \Sigma X \Sigma Y}{M \Sigma X^2 - (\Sigma X)^2}$$

where:

X = μg/ml of metal added.
Y = peak height in chart divisions.
a = constant of least squares line.
b = slope of least squares line.
M = total number of measurements of peak height.

(4) Calculate the variance with respect to the straight line as follows. (Note: Calculation Steps 4, 5, and 6 are optional if all data points are within ± 5 divisions of the least square line.)

$$S_0^2 = (\Sigma Y^2 - \overline{Y} \Sigma Y - b\,(\Sigma XY - \overline{X} \Sigma Y))/(M - 2)$$

wherein:

S_0^2 = variance of Y values about the straight line.
$\overline{X}$ = mean of μg/ml of metal added.
$\overline{Y}$ = mean of peak heights.

Obtain the standard deviation S_0 by taking the square root of S_0^2.

(5) Plot peak height vs. μg/ml of metal added, plot the least-squares line, and plot on either side of the least squares line two lines which represent two standard deviations from the least squares line. Reject any peak heights that lie outside the acceptable limits.

(6) Repeat Calculation Steps 3, 4, and 5 until all points are within the acceptable limits.

(7) Calculate the concentration of metal in the original sample as follows:

The equation of the least squares line is

$$Y = a + bX$$

Set $Y = O$ then

$$X = -a/b$$

where:

X = μg/ml of metal in the original 10-ml solution of digestate (ignore the sign).

Thus,

$$\text{ng Mo/g in sample} = \frac{(10)\,(1000)\,(X)}{W}$$

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where:

W is the weight of sample.

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14

Nickel and Vanadium

Up to several thousand parts per million of nickel and vanadium may be present in crude petroleum as metal porphyrin and other complexes. Although most of it in a crude oil remains in the residual fractions and coke during refining, minute quantities have been observed in distillate fractions (*1*). Since nickel and vanadium are the most widely analyzed trace metals in petroleum, the Project addressed itself only to the sub part-per-million levels.

Available Analytical Methods. The most commonly used colorimetric reagent for nickel—dimethylglyoxime—can be used to measure levels of nickel as low as 20 ppb after appropriate preconcentration (*2*). For vanadium, hematoxylin (*3*) and PAR-zephiramine (*4*) are sensitive colorimetric reagents that can be used to measure as little as 0.1 and 0.015 ppm, respectively. However, a number of elements interfere, and they must be removed prior to measurement.

X-ray fluorescence spectroscopy has been used to determine 50 ppb of nickel and vanadium after they have been concentrated on ion exchange resins (*5*, *6*). Emission spectroscopy has been used but is only semiquantitative at the nanogram/gram levels of interest to the Project. Nevertheless, the technique may be useful as a screening tool. Two relatively new instrumental techniques—spark source mass spectrometry (*7*) and kinetics of metal-catalyzed reactions (*8*)—can measure extremely low levels of nickel and vanadium, but they have not been utilized to any appreciable extent.

Flame atomic absorption is sensitive enough to measure part-per-billion levels of nickel in aqueous solution, but it is not that sensitive for vanadium. Heated vaporization atomic absorption is more sensitive, permitting detection of vanadium down to 20 ng/ml in aqueous solution. Therefore, for the practical quantitative determination of nanogram/gram concentrations of both nickel and vanadium in petroleum, the combination of HVAA with a preconcentration ashing step was selected for detailed study.

Role of Neutron Activation. Thermal neutron activation does not produce a suitable gamma-emitting isotope for measuring nanogram/gram levels of nickel. For vanadium, the ^{51}V (n,γ) ^{52}V reaction, producing a 1434-KeV gamma-ray peak, may be used to measure 10 ng V/g and is not subject to any interferences. However, the half-life of the ^{52}V isotope is

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only 3.8 min, so that pneumatic sample transfer from the reactor core to the counting facilities is essential.

Special Analytical Considerations. Loss of nickel and vanadium when petroleum samples are dry ashed is well known. Similar losses occur if the HVAA technique is applied directly to some petroleum fractions (9). Losses of this type are particularly serious with the distillate materials studied by the Project since the volatile porphyrins are found in these fractions. Sulfuric acid has been recommended as a suitable decomposition procedure for samples containing volatile nickel and vanadium, and this approach was investigated. However, other decomposition procedures designed to prevent loss of nickel or vanadium, in which the sample is heated with either benzenesulfonic acid (*10*) or sulfur (*11*), were not investigated.

Although no contamination from apparatus or reagents was found for vanadium, several sources of contamination were encountered for nickel. High purity sulfuric acid contained 4–5 ng Ni/ml while the hydrochloric acid did not contain any measurable amount. Vycor dishes which had been used previously retained traces of nickel that were significant when nanogram quantities were being determined. Even after thorough washing, such dishes could not be used confidently. New glassware should be used and preferably dedicated exclusively for the tests at this level. New vessels must be cleaned carefully before use. The data in Table 14.I show the nickel contamination resulting from two new dishes that had been previously used once to decompose samples containing part-per-million levels of nickel. The nickel contamination was eliminated only after several 5-ml portions of concentrated sulfuric acid were taken down to fumes in the dish; the 20-30 ng of remaining nickel represented the reagent blank.

Table 14.I. Nickel in Solution after Successive Acid Washing of 800-ml Vycor Dishes

Treatment	*Nickel Content (ng)* Dish 1	*Nickel Content (ng)* Dish 2
(1)[a] 10 ml 1:1 HCl only	157	92
(2)[b] 5 ml conc. H_2SO_4 + 10 ml 1:1 HCl (1)	74	55
(3) First repeat of (2)	34	19
(4) Second repeat of (2)	23	24
(5) Third repeat of (2)	29	24

[a] Boiled, evaporated to dryness on the steam bath, and the residue taken up in 10 ml 1:19 HCl.

[b] Taken to fumes of conc. H_2SO_4, 1:1 HCl added, then treatment (1).

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To test the treating procedure, several fuels were analyzed for nickel by our recommended method, using both (1) treated and (2) washed but untreated Vycor dishes. The results, which are compared in Table 14.II, show that contamination is eliminated by the consecutive fumings with the acid.

Table 14.II. Nickel in Fuels by HVAA

	Nickel Concentration (ng/g)	
Sample	*Untreated Vycor Dishes*	*Treated Vycor Dishes*
Gasoline	12, 5, 13	$< 2, < 2$
Jet Fuel	7, 16	$< 2, < 2$
No. 2 heating oil	21, 9	11, 9

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Sample Preparation. The procedure described by Milner et al. (*12*), based on wet ashing with sulfuric acid and incineration in a Vycor dish, was adopted without modification for the decomposition of middle and heavy distillates. For light distillates (i.e., gasolines) the decomposition time was shortened considerably by evaporating the sample in a stream of nitrogen after the sulfuric acid addition but before the incineration.

Measurement. Optimum HVAA parameters were established empirically for standard dilute hydrochloric acid solutions of the metals. The heat retained by the tube furnace between cycles affects the repeatibility of successive injections. Although injections were made on a fixed time schedule, multiple injections were usually necessary to obtain reliable readings.

It is important to establish that the ash cycle settings used do not cause loss of nickel by premature volatilization. Campbell and Ottaway (*13*) reported that when aqueous nickel sulfate solutions were injected, 12–26% of the nickel was lost at an ashing temperature of 750°C for 300 sec. At the power and time settings used in the Project, it was demonstrated that no metal was volatilized prematurely.

The existence of background (non-atomic) absorption at the analytical wavelengths for Ni (232.0 nm) and V (318.5 nm) was investigated using a hydrogen continuum lamp. Under the conditions used, the background signals for the samples were indistinguishable from the baseline. Consequently, no background correction is required in the procedure. Furthermore, under the conditions for atomization, the maximum response was obtained with no "memory" from one atomization to the next.

The high temperature required to atomize the vanadium lowers the life of the atomization furnaces, and it is recommended that the furnace be replaced after 20–25 injections. Good contact between the support electrodes and the furnace must be maintained. This is particularly critical for vanadium because maximum power is required to ensure

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complete atomization. Even a small loss of power by poor contacts may substantially reduce the temperature inside the furnace.

Under the specified conditions, the calculated detection limits (S/N = 2) for nickel and vanadium are 2×10^{-11} g and 25×10^{-11} g, respectively. With these limits, it was possible to measure 2 ng Ni/g, and 5 ng V/g in an original 100-g petroleum sample, using respective 1- and 5-μl aliquots of the final solution for injection. Response was linear over the range 0–1 ng Ni and 0–10 ng V.

Matrix effects were encountered in the HVAA measurement of nickel and vanadium. The response when a mixture of 14 metals was added in various ratios to a constant concentration of nickel and vanadium is shown in Table 14.III. When the concentration of each interfering metal was the same as nickel, the change in the nickel response was insignificant. However, as the concentration of interfering metal was increased, the nickel response was significantly enhanced. For vanadium, the response was significantly depressed, even when the concentration of each interfering metal was the same as the vanadium concentration. Although no explanation for the behavior of nickel and vanadium in the presence of other metals has been found, the nickel and vanadium calibration curves are linear, indicating that the method of standard additions can be utilized.

Even with the precautions noted above, response from vanadium was often quite variable. Consequently, the slope and intercept of response vs. μg/ml of standard addition were calculated by the method of least squares. The standard deviation of the response about the regression line was also calculated, and any data points outside 2σ of the regression line were rejected. The slope and intercept were then recalculated, and the

Table 14.III. Effect of Other Metals on the Determination of Nickel and Vanadium[a, b]

	Nickel			*Vanadium*		
Concentration of Each Interfering Metal,[c] *μg/ml*	*Avg. Response, mm*	*Std. Dev. of Response, mm*	*No. of Measurements*	*Avg. Response, mm*	*Std. Dev. of Response, mm*	*No. of Measurements*
0	50	5	9	36	4	12
0.5	53	2	3	29	4	8
5	65	3	3	20	4	8
50	89	10	3	19	3	6

[a] Concentration of Ni or V in solution: 0.5 μg/ml.
[b] Amount injected: 2 μl for Ni, 5 μl for V.
[c] Interfering metals present: Si, Al, Cr, Ca, Fe, Mg, Na, Mn, Zn, Cu, Co, Pb, Mo, Ni, or V.

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concentration of vanadium in the sample solution was obtained by extrapolating the "refined" regression line. In all determinations the regression line was statistically tested for linearity. The response when nickel was atomized varied less than that of vanadium, so the nickel concentration in the sample solution could be calculated either by least squares or the equation on p. 170.

Recommended Method. In the recommended method a 100-g sample is decomposed with concentrated sulfuric acid, ashed at 500°C, dissolved in dilute hydrochloric acid, and the concentration of nickel or vanadium measured by HVAA using the method of standard additions. The results of applying this procedure to several distillate fuels are shown in Table 14.IV. Each material was spiked to contain different levels of nickel and vanadium, which were added as the sulfonates. Essentially quantitative recoveries were obtained for both nickel and vanadium from all materials. The standard deviation for nickel was ± 6 over the range 50 to 100 ng Ni/g, and for vanadium ± 8 ng V/g over the range 30–100 ng V/g. The few tests at the higher level indicated a comparable precision.

Samples of gasoline, jet fuel, and No. 2 heating oil were spiked with nickel and vanadium sulfonates and, together with unspiked samples, were analyzed at the initiating laboratory and at one cooperating laboratory. The results on the spiked samples at the cooperating laboratory were, on the whole, lower than those of the initiating laboratory (Table 14.V), although the precision was identical.

The lower recovery at the cooperating laboratory is attributed to a time lag in the analysis. The cooperating laboratory analyzed the samples about four months after they were prepared, whereas the initiating laboratory analyzed the samples immediately. A separate long-term stability study demonstrated that nickel and vanadium sulfonates in kerosene were gradually depleted in storage (Figure 14.1), and the delay in performing

Table 14.IV. Recovery of Nickel and Vanadium in Distillate Fuels by HVAA Method

	Nickel Concentration (ng/g)			*Vanadium Concentration (ng/g)*		
Sample	*Added*	*Measured*[a]	*% Recovery*	*Added*	*Measured*[a]	*% Recovery*
Diesel fuel	53	56	100	35	41	117
	95	93	95	72	74	103
Kerosene	104	106	102	109	98	90
Gasoline	234	208	89	468	467	100

[a] Average of triplicate determinations.

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Table 14.V. Interlaboratory Analysis for Nickel and Vanadium by Proposed Method

	Nickel Concentration (ng/g)			*Vanadium Concentration (ng/g)*		
	Added	*Measured*[a]		*Added*	*Measured*[a]	
Sample		*Initiating Laboratory*	*Cooperating Laboratory*		*Initiating Laboratory*	*Cooperating Laboratory*
Gasoline	0	< 2	8	0	< 5	< 5
	34	32	28	26	25	23
Jet fuel	0	< 2	< 2	0	< 5	< 5
	64	63	44	40	43	31
No. 2 heating oil	0	10	10	0	< 5	< 5
	31	45	28	58	56	53

[a] Average of triplicate results.

the analyses probably caused the difference between the results. Despite the apparently low recoveries obtained by the cooperating laboratory on the synthetic sample, the good precision indicates that the method should be reliable for field samples.

Detailed Procedure

Scope. The method is used to determine nickel and vanadium in petroleum and petroleum products at levels of 2–10 ng Ni/g and 5–500 ng V/g. Six to twelve samples can be processed conveniently in a batch, with a total working time of 12 hr when both metals are determined.

Summary of Method. A large sample (100 g) is decomposed by heating with sulfuric acid. The resulting carbonaceous residue is ashed in a muffle furnace at 500°C. The ash is dissolved in dilute hydrochloric acid and diluted to 10 ml. The concentration of each metal is measured on 2-ml aliquots of the digestate by heated vaporization atomic absorption, using the method of standard additions.

Apparatus

(1) *Atomic absorption spectrometer,* Varian-Techtron AA5 or equivalent.

(a) Strip chart recorder, 0-10 mv with 0.5-sec response time, Leeds & Northrup Speedomax W or equivalent.

(b) Nickel hollow cathode lamp, Varian-Techtron or equivalent.

(c) Vanadium hollow cathode lamp, Varian-Techtron or eqiuvalent.

(d) Hydrogen hollow cathode lamp. Varian-Techtron or eqiuvalent.

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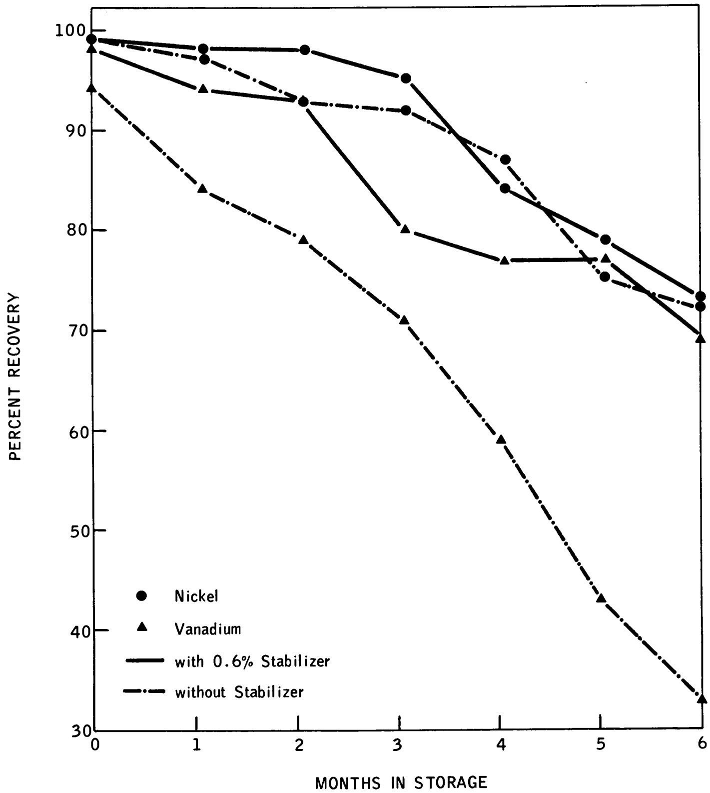

Figure 14.1. Stability of nickel and vanadium sulfonates in kerosene; 100 ng/g metal added

(2) *Carbon rod atomizer,* model 63, Varian-Techtron or equivalent.

(a) Pyrolytic-graphite coated atomization furnaces, Varian-Techtron or equivalent.

(b) Support electrodes manufactured by Ringsdorff-Werke, GMBH, type RW 0124 (Varian-Techtron).

(3) *Vycor dish.* Cut an 800-ml beaker to a 10-cm height. It is strongly recommended that new dishes be prepared and used exclusively for this work. All Vycor dishes must be cleaned by the following procedure before use. Add 50 ml of 1:1 HCl and boil for 10 min. Discard the HCl solution and take three successive 5-ml portions of concentrated sulfuric acid to fumes in the dish. Finally, wash the dish with water and air dry.

(4) *Air bath.* Cut a cylinder of aluminum with a diameter slightly larger than that of the dish to a 9.5-cm length.

(5) *Infrared Lamp,* 250-watt, supported about 2.6 cm above the air bath.

(6) *Variable transformer* to regulate the heat of the infrared lamp.

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(7) *Muffle furnace,* capable of maintaining 500° ± 25°C and equipped with a supplementary air or oxygen supply.

(8) *Syringes.* 1-, 5-, 10-, and 100-μl with Teflon tips.

(9) *Volumetric flasks,* 5- and 10-ml.

Reagents. Unless otherwise indicated, reagents are ACS reagent grade. Water is deionized.

(1) *Sulfuric acid,* concentrated (high purity).

(2) *Hydrochloric acid,* dilute. Add 50 ml of concentrated acid to 950 ml of water.

(3) *Standards*

(a) Stock standards. Aqueous nickel and vanadium standards, 1000 ppm (Fisher Scientific, etc.)

(b) Calibrating standards. Prepare 50 ml of the following calibration standards by careful successive dilutions starting with the 1000-ppm standards:

vanadium	50 μg/ml
nickel	10 μg/ml

These calibration standards must be prepared immediately before use.

Procedure

(1) *Instrument operation.* Use the parameters listed in the table below as a guide in optimizing the instrument and carbon rod atomizer.

(a) Set up the AA spectrometer and carbon rod atomizer to measure nickel.

(b) Set up the AA spectrometer and carbon rod to measure vanadium after the nickel measurements are complete.

Operating Conditions	*Ni*	*V*
Wavelength, nm	232.0	318.5
Lamp current, ma	5	20
Slit, μm	50	50
Inert gas	Argon	
flow rate	3 l/min	
pressure	15 psi	
Injection frequency	90 sec	

CRA-63 Program

	Ni		*V*	
	Supply Setting	*Sec*	*Setting Supply*	*Sec*
Dry (initial	3.0	10	3.0	10
Dry (final)	20	10	20	10
Ash	6.5	15	8.0	15
Atomize	8.5	5.0	9.5	6.0
Typical response (absorbance/ng)	0.25		0.05	

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(2) *Sample decomposition*

(a) Carry a reagent blank through the procedure, starting with 5 ml of sulfuric acid.

(b) Weigh 100 g of sample into a Vycor dish. Add 5 ml of concentrated sulfuric acid, mix with a glass stirring rod, and place the dish in an air bath. Place the bath on a hot plate and suspend an infrared lamp above the dish so that the face of the bulb is 2.6–5.2 cm above its top. For light matrices such as gasoline, most of the sample should first be evaporated with a stream of nitrogen before the dish is placed in the air bath.

(c) Heat the sample with the lamp and then with low heat from the hot plate. Stir frequently with a glass rod to break up any surface crust and reduce spattering. Increase the heat gradually until fumes of sulfuric acid are no longer evolved, transfer the dish to the muffle furnace at 500°C, turn on the air or oxygen supply, and ash the residue.

(d) Cool, wash down the walls of the dish with 5 ml of dilute hydrochloric acid, cover, and dissolve the ash by warming on the steam bath. Transfer the solution quantitatively to a 10-ml volumetric flask, dilute to volume with dilute hydrochloric acid, and mix thoroughly.

(e) Transfer accurately two 2-ml aliquots of each digestate (ignore any precipitate) to 5-ml volumetric flasks. Use one for the nickel determination and the other for the vanadium determination.

(3) *Measurement of nickel*

(a) Insert a new tube furnace between the support rods and set up to measure nickel with the recorder set at 5 mv full scale. Clean the atomization furnace by "baking" at maximum temperature several times until an acceptable blank is obtained.

(b) Set the dry, ash, and atomize conditions to the appropriate settings.

(c) Withdraw a 1-μl aliquot of a digestate.

(d) Initiate the atomization program and immediately inject the sample aliquot. After 10 sec from program initiation, increase the dry cycle voltage control to its maximum and allow the program to run to completion. Reset the dry cycle voltage to its original setting.

(e) Record the peak height caused by absorbance observed during the atomization step of the program.

(f) From the peak heights obtained, select an aliquot of digestate such that the peak height is 10–20 divisions above the blank and background signal. Also select an aliquot of calibration standard such that the peak height (after the third addition) will be about four times the peak height for the original digestate. Use these same aliquots throughout the determination of that sample.

(g) Withdraw the selected aliquot of digestate into a microliter syringe and follow Steps d and e. Repeat twice more. If the three signals are within ± 10% of their average, continue to Step h. Otherwise, repeat Steps d and e twice more and average the five readings.

(h) Add the selected aliquot of calibration standard solution to the digestate and mix well. Carry out Step g.

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(i) Add another aliquot of the calibration standard to the solution from Step h and repeat Step g.

(j) Add another aliquot of the calibration standard to the solution from Step i and again repeat Step g.

(4) *Measurement of vanadium.* When determining vanadium, it is recommended that the tube furnace be discarded after 25–30 peak height measurements. Do not change the furnace in the middle of set of peak height measurements on a sample digestate.

(a) Measure the vanadium, following Steps b–j above, but using a 5-μl aliquot of the digestate.

Calculation

(1) Calculate the concentration of each standard addition in μg/ml.

(2) Tabulate the peak height measurements in chart divisions obtained from the digestate and digestate plus standard additions. Subtract the peak height obtained on the blank solution from the sample peak heights.

(3) Calculate the best straight line by least squares by the equations:

$$a = \frac{\Sigma Y \Sigma X^2 - \Sigma X \Sigma XY}{M \Sigma X^2 - (\Sigma X)^2}$$

$$b = \frac{M \Sigma XY - \Sigma X \Sigma Y}{M \Sigma X^2 - (\Sigma X)^2}$$

where:

X = μg/ml of metal added.
Y = peak height in chart divisions.
a = constant of least squares line.
b = slope of least squares line.
M = total number of measurements of peak height.

(4) Calculate the variance with respect to the straight line as follows. (Steps 4, 5, and 6 are optional if all data points are within ± 5 divisions of the least square line).

$$S_0{}^2 = \frac{(\Sigma Y^2 - \overline{Y}\Sigma Y - b\ (\Sigma XY - \overline{X}\Sigma Y))}{(M - 2)}$$

where:

$S_0{}^2$ = variance of Y values about the straight line.
$\overline{X}$ = mean of μg/ml of metal added.
$\overline{Y}$ = mean of peak heights.

Obtain the standard deviation S_0 by taking the square root of $S_0{}^2$.

(5) Plot peak height vs. μg/ml of metal added, plot the least-squares line, and plot on either side of the least-squares line two lines which represent two standard deviations from the least-square line. Reject any peak heights that lie outside the acceptable limits.

(6) Repeat Steps 3, 4, and 5 until all points are within the acceptable limits.

(7) Calculate the concentration of metal in the original sample as follows. The equation of the least-squares line is:

$$Y = a + bX$$

Set $Y = 0$, then:

$$X = -a/b$$

where $X = \mu g/ml$ of metal in the original 10 ml solution of digestate (ignore the sign).

Thus,

$$\text{ng/g metal in sample} = \frac{(10)(1000)(X)}{W}$$

where W is the weight of sample.

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15

Selenium

Selenium and sulfur frequently occur together in nature, and both elements form volatile compounds upon combustion. Consequently, fossil fuels, which frequently contain sulfur, can also contain traces of selenium, and combustion of these fuels could contribute significant amounts of selenium to the atmosphere. As a result, the determination of selenium in petroleum and petroleum products is of considerable importance.

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Available Analytical Methods

Macro quantities of selenium can be determined gravimetrically after reduction to the elemental form by various reagents such as tin(II) chloride, potassium iodide, or ascorbic acid (*1*). Ooba described a technique whereby the element is precipitated from perchloric acid solution with hydrazine (*2*). Selenium may be titrated with standard solutions of sodium thiosulfate, iodide, and ferrous, chromous, or trivalent titanium salts after oxidation to Se(VI) (*1*). Photometric and fluorometric methods based on formation of the piaselenol with diaminobenzidine or 2,3-diaminonaphthalene has been used for the determination of selenium (*1, 3, 4, 5*). Interfering elements such as As, Co, Cr, Cu, Fe, Hg, and Ni, are masked with EDTA or other chelating agents.

Atomic absorption techniques, combined with hydride generation, have been widely adopted (*6, 7, 8*), probably because of the ready availability of atomic absorption instruments, the simplicity of the technique, and the relative freedom from interferences. In the general technique used, the selenium is reduced and liberated as hydrogen selenide in one of several ways: (1) by reaction with tin(II) chloride and zinc in acid solution, (2) by reduction with zinc and acid alone, or (3) by reduction with sodium borohydride. The H_2Se is swept from the system by the stream of H_2 generated by the zinc or by a supplementary flow of argon into an argon–hydrogen entrained air flame or a heated furnace and measured by atomic absorption. Alternately, it can be collected in liquid nitrogen cold trap and a balloon and measured later. During the Trace Metals Project each technique was evaluated. The technique whereby the H_2Se is generated by zinc in acid and conveyed

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directly into an argon–hydrogen air entrained flame was established as the preferred method of measurement.

Role of Neutron Activation

Activated selenium [(^{74}Se (n,γ) ^{75}Se)] yields two measurable gammas (265 and 136 KeV) that are not interfered with by typical components of crude oils or petroleum products. However, extended irradiation and counting times are required to reach a 10 ng/g detection limit.

Special Analytical Considerations

During the Trace Metals Project it was established that some lots of acids were relatively free of selenium and could be used without further purification. Other lots of the same acid contained unacceptable concentrations of selenium and had to be purified before use. A sub-boiling distillation procedure (9) was found suitable for purifying the acids that are required for the sample decomposition and selenium measurement. Although contamination from sulfuric acid was expected because of the frequent association of selenium with sulfur, most lots tested could be used without purification. Since others have reported severe contamination (*10*), it is advisable to screen sulfuric acid lots carefully before use. Selenium could not be generated when one lot of unpurified perchloric acid was used, but it could be quantitatively generated after that lot had been purified by the sub-boiling distillation technique.

Selenium has been reported to be completely lost from organic samples when subjected to dry ashing techniques (*11*). As part of the Trace Metals Project, ashing studies were carried out which confirmed the loss for dry ashing of petroleum matrices. When ashing aids such as sulfur or magnesium oxide were used, some selenium was retained in the ash, but the recovery was not complete.

Most selenium measurements are complicated by the presence of other elements in the sample. In some cases selenium can be separated from interferences by distillation as the bromide, by high pressure liquid chromatography, or by solvent extraction (*1, 12, 13*). The hydride generation technique provides good separation of selenium from interferences in the atomic absorption technique that has been developed. However, separation from arsenic and mercury is not accomplished, and these elements and the nitrate ion have been found to interfere (*14, 15*). However, the effect of these species on the measurement is not significant for the method developed by the Project.

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Sample Preparation

During the Trace Metals Project several sample preparation techniques were evaluated for the determination of selenium in petroleum and petroleum products. Wet oxidation under reflux was the technique adopted because it was the only one that gave quantitative recovery of selenium from various petroleum-type samples. Some of the techniques that were evaluated are discussed below.

Wet Oxidation under Reflux. The sample is mixed with concentrated sulfuric acid in a Kjeldahl flask, and a water-cooled spiral condenser is attached (Figure 15.1). Nitric acid is added through the condenser, and the mixture is stirred and heated in stages. After the bulk of the

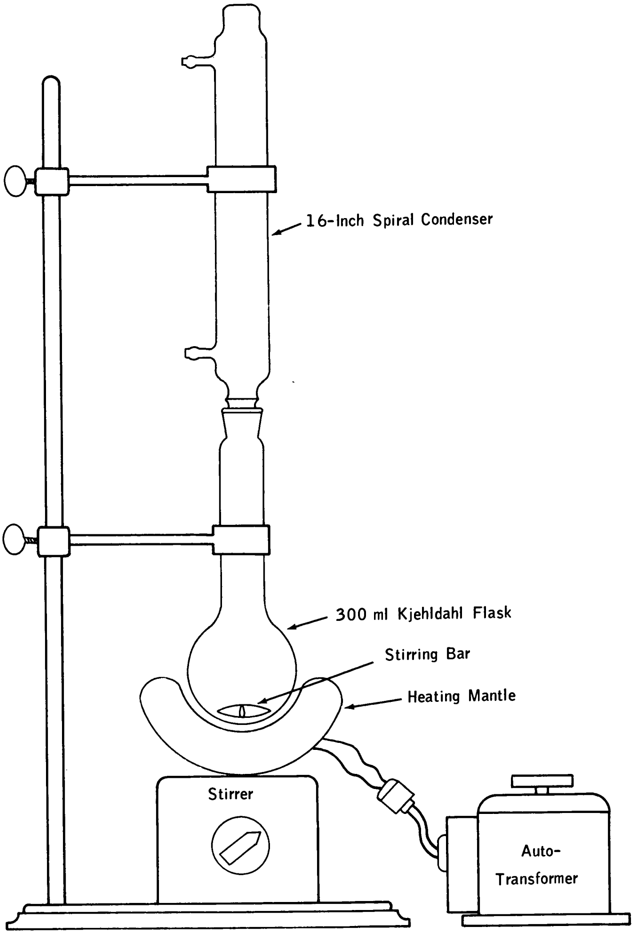

Figure 15.1. Wet oxidation apparatus

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organic material is destroyed, perchloric acid is added through the condenser to complete the oxidation. The condenser is removed, and the excess nitric acid is eliminated by taking the solution to fumes of sulfuric acid. Remaining traces of nitric acid are removed by the addition of sulfamic acid.

Quantitative recovery of selenium was verified for a gasoline sample spiked with a known amount of selenium as dilaurylselenide and a mineral oil (white oil) spiked with dilaurylselenide and selenium dioxide. The samples were oxidized under total reflux, and the selenium was measured by the hydride generation–atomic absorption technique. Quantitative recovery of the added selenium indicated that selenium is not lost during sample preparation (Table 15.I).

Wet Oxidation–Open Flask. Rapid and generally complete oxidation of the organic material was obtained when a 1-2 g sample was mixed with 10 ml of concentrated sulfuric acid in an open Kjeldahl flask and concentrated nitric acid was added dropwise to the warm mixture. The last traces of organic material were destroyed by the dropwise addition of perchloric acid. Quantitative recovery of the selenium was obtained when the oxidation was carried out without charring the sample. However, it was extremely difficult to control since charring occurred as the result of variations in the drop rate of the nitric acid, in the type of sample, and in the rate of heating. Thus, each sample required constant attention.

Wickbold Combustion. Recoveries approximating 50% were obtained by the combustion of spiked crude oils in a Wickbold burner using either dilute hydrochloric acid or hydrogen peroxide as the absorbing solution. Subsequent studies suggested that the low recovery was caused by the loss of selenium through adsorption on the walls of the hot combustion tube. The losses by adsorption appeared to be independent of sample matrix and to occur in essentially all petroleum samples. Consequently, no further studies on the Wickbold combustion technique were carried out.

Raney Nickel Adsorption. Raney nickel can adsorb selenium and certain other elements from solution. It can be separated by filtration,

Table 15.I. Recovery of Selenium by Proposed Method

		Selenium Concentration (ng/g)	
Sample	*Form Added*	*Added*	*Measured*
Gasoline	dilauryl selenide	200	198
Mineral oil	"	54	52
"	"	108	114
"	selenium dioxide	50	62
"	"	100	98

dissolved in acid, and the selenium determined by the hydride generation–atomic absorption technique. By this technique up to 500 ng of selenium was recovered quantitatively from aqueous solutions by stirring the Raney nickel–aqueous selenium solution overnight. However, recovery was only 10–20% from crude oils that were spiked with known amounts of selenium. Recovery was improved to 80% by carrying out the adsorption in a bomb pressurized at 10 atm with hydrogen, but no further work was done with this approach.

Measurement

Two different, yet complementary, techniques were evaluated for selenium measurement. Both techniques are based upon hydrogen selenide generation and measurement of selenium by atomic absorption spectroscopy. In one, a hydrogen–argon entrained air flame is used; in the other, a flame-heated Vycor furnace is employed. Interlaboratory studies confirmed that for most samples either measurement system may be used. However, since linearity was not obtained with the flame-heated Vycor furnace for all sample types, the hydrogen–argon entrained air flame is the recommended method of measurement. In the procedure adopted by the Trace Metals Project, the hydrogen selenide is generated by adding zinc to a stirred acid solution containing selenium and is swept from the hydride-generating flask directly into the flame (Figure 15.2).

Hydride Generation. Hydride generation separates selenium from the generating (sample) matrix and from most other elements. The rate of hydride generation is affected by the acid composition of the generating solution. Maximum response is obtained with 0.4 equivalent of hydrochloric acid and 0.6 equivalent of sulfuric acid (Figure 15.3). This suggests that a HCl/H_2SO_4 equivalence ratio of about 0.67 is the optimum for maximum selenium response. A study of the effect of total acid ($HCl + H_2SO_4$) concentration on peak height and peak area response indicated that the maximum response is obtained with a total acid concentration of about 70% (Figure 15.4). Although the response depends on acid ratio and total concentration, it is independent of the volume of generating solution from which the hydrogen selenide is generated (Figure 15.5). Volumes less than 40 ml are difficult to stir adequately, and volumes larger than 100 ml tend to foam over during hydrogen selenide generation. The following conditions are considered to give the optimum response for selenium: (1) a HCl/H_2SO_4 equivalence ratio of about 0.67, (2) a total acid concentration of about 70%, (3) a total volume of 40–100 ml of generating solution, and (4) the addition of 7 g of zinc dust. Under these conditions, comparable response is obtained for either Se(IV) or Se(VI).

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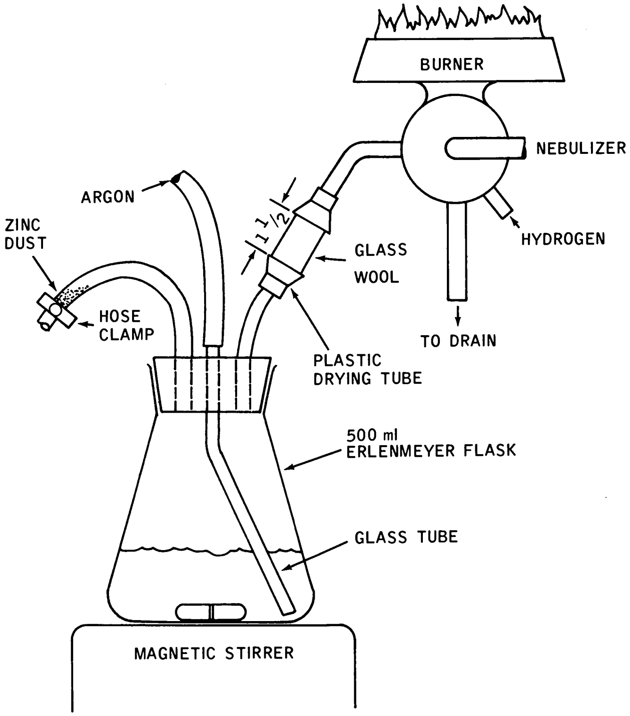

Figure 15.2. Selenide generation apparatus

Measurement of Response. Under the conditions described above, hydrogen selenide is introduced directly into the flame and produces a transient signal for 4–5 sec. Either the peak height or the peak area may be used as the selenium response. There is no significant difference in the precision between the two measurements (Table 15.II). Although either may be used as an indication of the selenium response, peak height was used for the measurements in the Project.

Interferences. Since the selenium is removed from the aqueous (sample) matrix as hydrogen selenide prior to measurement, possible interference would be expected to be limited to the volatile elements, to those elements that form hydrides, and to any species which affects the rate of generation. Although arsenic forms a hydride under the specified conditions, no interference was observed when either As(III) or As(V) was added at levels as high as 10 μg/ml. Mercury, which could be evolved under the reducing conditions used, was not studied but rarely is found in petroleum matrices in significant quantities. Selenium response was unaffected by the presence of 13 elements (Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and V) when each was present in a concentration ratio of 100:1 with respect to the selenium.

Table 15.II. Precision of Flame Measurement Step

Selenium, ng	*Coefficient of Variation*
100	10
150	12.6
250	12.5
500	3.3

The response for the first eight to 10 measurements at the start of each day was significantly lower than subsequent measurements (Figure 15.5) and could not be used for quantitation. However, after the first eight to 10 measurements, both the peak height and peak area become constant and reproducible. No explanation for this drift has been found. To avoid its effect, the system must be preconditioned by generating H_2Se from eight to 10 selenium standards before collecting data.

Recommended Method

The organic matrix is destroyed by wet oxidation under reflux conditions with sulfuric, nitric, and perchloric acid. Nitrate which interferes with hydrogen selenide generation, is removed, the acid concentration is adjusted, and the selenium is converted to hydrogen selenide by the

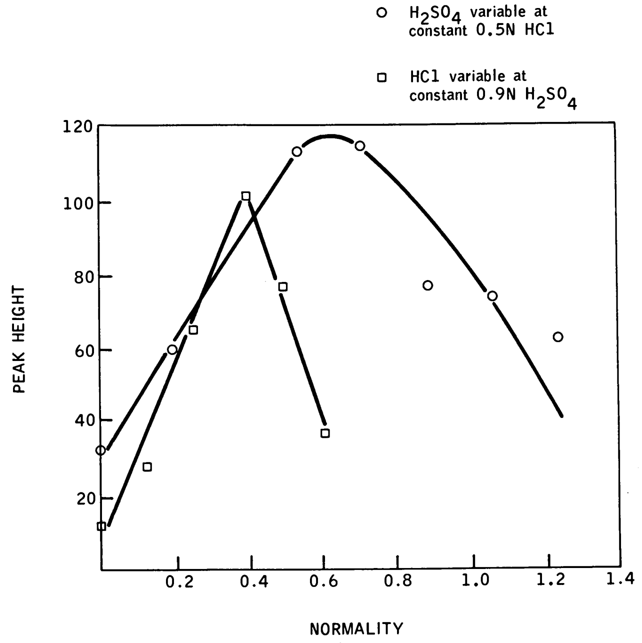

Figure 15.3. Effect of HCl and H_2SO_4 on peak height of selenium

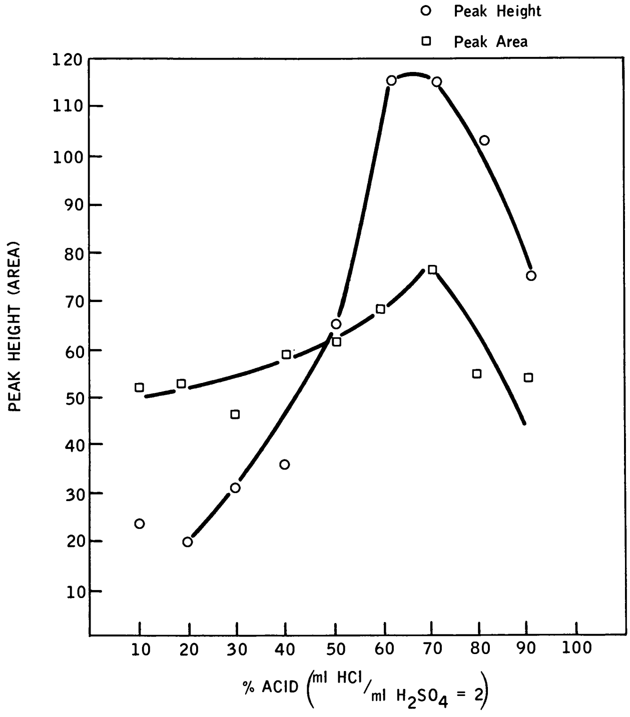

Figure 15.4. Effect of total acid concentration on peak height and area

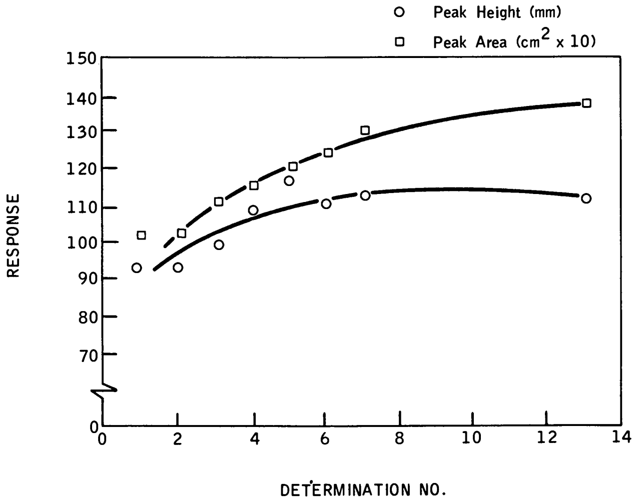

Figure 15.5. Updrift in selenium response

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Table 15.III. Recovery of Selenium by Proposed Method

Sample	*Selenium Added (ng/g)*	*Form*	*% Recovered*
No. 2 heating oil	100	dilauryl selenide	94
Gasoline	110	"	96
Crude	200	"	91
White oil	54	"	76
"	108	"	94
"	162	"	108
"	50	selenium dioxide	130
"	50	"	104
"	100	"	105
"	100	"	90
"	150	"	107

addition of zinc. The hydrogen selenide is introduced directly into the hydrogen–argon entrained air flame, and the selenium is measured by atomic absorption spectroscopy.

The precision of the flame measurement step was established using aqueous calibration standards (Table 15.II). The accuracy of the method was evaluated using various petroleum materials spiked with selenium dioxide and dilaurylselenide. The results (Table15.III) show an average recovery of 100% and suggest that the method is accurate within the precision of the measurement.

To validate the accuracy of the procedure further, five petroleum samples, including four that contained native selenium, were analyzed in three laboratories by different methods. One laboratory used the flame-heated Vycor furnace measurement technique, another used the hydrogen entrained air flame, and the third used neutron activation (Table 15.IV).

Table 15.IV. Interlaboratory Cross-Check Results

	Selenium Concentration (ng/g)			
	Added	*Measured*		
Sample		*Laboratory 1*[a]	*Laboratory 2*[b]	*Neutron Activation*
Gasoline	0.0	< 10	< 10	—
Gasoline	105	110	103	—
No. 2 fuel oil	0.0	17	< 18	15
No. 2 fuel oil	105	122	109	110
No. 6 fuel oil	0.0	137	130	144
Crude A	0.0	125	—	124
Crude B	0.0	29	27	—

[a] Measurements made with flame heated Vycor furnace.
[b] Measurements made with hydrogen–argon air entrained flame.

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The results obtained with the flame-heated Vycor furnace and hydrogen–argon entrained air flame are in excellent agreement with each other and with the results obtained by neutron activation. The results on the two samples that were spiked with a known amount of selenium, as dilaurylselenide, show quantitative recovery and suggest that both the flame-heated Vycor furnace or hydrogen–argon entrained air flame will provide reliable analyses of petroleum materials. However, the flame method is recommended, because the response was linear.

The recommended procedure is readily adaptable to any laboratory with atomic absorption capabilities. However, considerable experience with the procedure is required before valid results can be obtained. It is recommended that a sample of known selenium concentration be analyzed until the necessary skills are developed, before attempting to analyze samples of unknown selenium concentration.

Detailed Procedure

Scope. This method is used to determine selenium to the 10 ng/g level in petroleum and petroleum products.

Summary of the Method. The sample is oxidized under reflux conditions with sulfuric, nitric, and perchloric acid, and the selenium is measured as hydrogen selenide by hydrogen–argon entrained air flame atomic absorption.

Apparatus and Instrumentation

(1) *Apparatus for sample preparation* (*see* Figure 15.1).

(a) Kjeldahl flask, 300-ml with 24/40 female standard taper joint.

(b) Heating mantle, to accommodate a 300-ml Kjeldahl flask.

(c) Spiral condenser, 16-inch with 24/40 male standard taper joint.

(d) Variable auto-transformer, 140 V.

(e) Magnetic stirrer, variable speed.

(f) Magnetic stirring bar, 20 × 18 mm oval shaped.

(2) *Hydrogen selenide generating apparatus,* (*see* Figure 15.2).

(a) Erlenmeyer flask, 500 ml. Bore a 15-, 10-, and 8-mm hole in the rubber stopper. Insert a 10-cm long, 7/16-id Tygon tube through the top of the 15-mm hole. Clamp the free end with a hose clamp. Insert a bent 8-mm glass tube through the 8-mm hole and connect the top end to the argon supply with a 0.7 cm-id Tygon tube. Insert a 20-cm long, 0.7 cm-id Tygon tube through the 10-mm hole and attach the other end to the drying tube. Fill the drying tube loosely with glass wool and connect the drying tube to the oxidant inlet of the burner with 0.7 cm-id Tygon tube.

(3) *Instrumentation*

(a) Atomic absorption spectrophotometer, Perkin-Elmer model

403, or equivalent, equipped with background corrector, three-slot burner, and selenium hollow cathode lamp.

(b) Recorder, variable range and 0.5-sec full scale response.

(c) Pressure regulators, two-stage: one for hydrogen and one for argon.

Reagents. All reagents listed are ACS reagent grade. Water is understood to be distilled and deionized.

(1) *Sulfuric acid,* concentrated.

(2) *Hydrochloric acid,* concentrated.

(3) *Perchloric acid,* 70–72% (concentrated).

(4) *Nitric acid,* concentrated.

(5) *Zinc,* metallic dust.

(6) *Sulfamic acid,* 99%.

(7) *Hydrogen selenide generating solution.* Add 320 ml of water to a 1-liter flask. Cool in an ice bath and add slowly, and with caution, 290 ml of sulfuric acid and 390 ml of hydrochloric acid.

(8) *Standards*

(a) Selenium calibration standard, 1,000 μg/g (aqueous) Fisher Certified atomic absorption standard or equivalent.

(b) Calibration standard. Prepare calibration standards that contain 0.05, 0.1, 0.15, 0.2, and 0.3 μg of selenium per 100 ml of solution by serial dilution of the selenium calibration standard (above) with the hydrogen selenide generating solution.

Sample Preparation. Prepare all samples in duplicate. Carry reagent blanks through the entire procedure.

(1) Weigh 1.00 ± 0.01 g of sample into a 300-ml Kjeldahl flask.

(2) Add 10 ml of sulfuric acid, a magnetic stirring bar, and assemble the apparatus as shown in Figure 15.1. Add 10 ml of concentrated nitric acid through the condenser, stir, and heat for 30 min at an auto-transformer setting of 35 V.

(3) Increase the auto-transformer setting to 70 V and heat for an additional 30 min. Raise the flask from the heating mantle, add 5.0 ml (7.5 ml for crudes and residua) of concentrated perchloric acid through the condenser and allow to drain into the sample. Heat at an auto-transformer setting of 100 V for 1 hr or until the solution is clear and amber in color.

(4) Turn off heat, add 20 ml of water through the condenser, allow to drain completely and remove condenser. Heat at an auto-transformer setting of 100 V until fumes of sulfruic acid appear, remove heat, add 0.1 g of sulfamic acid, cover flask with a beaker, and allow the solution to cool to room temperature.

(5) Add 19.0 ml of concentrated sulfuric acid. Add 32 ml of water and allow to cool. **(CAUTION).** Add 39 ml of concentrated hydrochloric acid, allow to stand for 10 min, and transfer to a hydrogen selenide generating flask (Figure 15.2).

Measurement

(1) The following instrument parameters for determining selenium

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with a Perkin-Elmer model 403 spectrophotometer with a hydrogen–argon entrained air flame may be used as a guide:

Analytical wavelength	1960 nm
Hollow cathode lamp current	13 ma
Background corrector	on
Slit	4
Recorder scale	2 mV full scale
Mode	absorbance
Hydrogen flow	14.5 liters/min
Argon flow	13 liters/min

(2) Place a magnetic stirring bar in the generating flask that contains the sample or calibration standard. Place 7.0 ± 0.1 g of zinc dust in the dosing tube and bend tube so that the zinc will not fall out when the rubber stopper is inserted into the generating flask. Insert the rubber stopper into the generating flask. Stir the solution and purge the flask with argon until a steady baseline is obtained. Add the zinc dust to the generating flask by bringing the zinc dosing tube to a vertical position.

(3) Record the signal until the recorder returns to the baseline. Remove the rubber stopper from the generating flask and proceed to the next sample or standard.

(4) Measure the peak height response for each sample, reagent blank, and standard.

(5) Subtract the appropriate blank to obtain the net selenium response.

Calculation

(1) Prepare a selenium calibration curve by plotting the net selenium response vs. nanograms selenium for each selenium standard.

(2) Relate the net selenium response for each sample to the calibration curve to obtain the nanograms of selenium in the sample.

(3) Divide the nanograms selenium in the sample by the sample weight to obtain the concentration of selenium, in ng/g (ppb), in the sample.

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