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The Sampling, Handling and Storage of Materials for Trace Analysis

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The sampling, handling and storage of materials for trace analysis

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Trace and ultra-trace analyses require the most extreme care from the analyst. Too often this care is reflected in an inordinate amount of attention to the instrumentation and a corresponding inattention to sampling, sample stability, sample storage, and chemistry before analysis. For many elements, the control of contamination or sample stabilization, or both, may become the limiting factors in the accuracy of an analysis.

Numerous sample handling problems in trace element analysis are described and suggestions are made for the control of these problems. Analogous arguments can be made for similar problems in trace organic analysis. Examples of successful methods of sample handling are taken from relevant research results at the National Bureau of Standards.

Introduction

Few will quarrel with the observation that analytical chemistry today is of fundamental importance to many of the physical, engineering and health sciences. Indeed, it is difficult to find a product or process that is not directly influenced by analytical measurement. Analytical chemistry as a science is burgeoning with the development of newer, more powerful instrumentation that has better sensitivity and selectivity.

The demand for analytical data of improved quality is also increasing as researchers discover new phenomena and interactions. These are indeed exciting times to be an analytical chemist and yet some disturbing trends are perceptible. Better instruments do not necessarily generate more accurate data, yet there often seems to an almost blind faith in the accuracy of a result produced by an instrument.

The National Bureau of Standards (N.B.S.) is often called upon to help resolve measurement problems resulting from inaccurate, irreproducible data that render inter-laboratory data comparisons all but futile. Today's instrumentation has capabilities for analysis that have often outstripped our knowledge of sample chemistry or handling. It seems obvious that instrumental methods must be standardized and well calibrated to produce accurate, comparable data. Yet all instruments must be presented with a representative, valid sample and too often this has not been so. Thus it becomes necessary to re-examine what is known about the chemistry of the sample and the analytical system.

The term 'trace analysis' is usually taken to mean the determination of concentrations below 100 $\mu g\,g^{-1}$. Today in inorganic analysis, the working concentrations may extend to considerably less than 1 $ng\,ml^{-1}$. For organic trace analysis, even lower concentrations may be determined. Sample chemistries at these levels are not a simple extension of techniques used at higher concentrations. This paper will review some of the techniques for inorganic trace analysis, many of which have analogous applications for trace organic analysis.

Sampling

Contamination during sampling may be a major problem in trace and ultra-trace analysis. The magnitude of the problem is a function of the difference between the concentration of the trace element in the sample and the concentration of the trace element in the contaminating media. It is also a direct function of the length of contact time between the sample and the contaminating medium (e.g. the sampling apparatus). Thus to minimize the effects of sample contamination, a guiding principle in almost all aspects of trace analysis is to choose a sampling medium (apparatus) with the least potential for contamination and the minimize the contact time of the apparatus with the sample.

Even with this precaution, it is still necessary to prove that the sample obtained is indeed representative of the material being sampled. For a clear liquid sample there is inherently less of a problem in sampling from a material that can easily be made homogeneous. For a granular, solid material, considerably more sample handling may be required to achieve a representative sample. This may involve grinding, blending and sieving before sampling, all of which may greatly increase contamination levels. Fortunately, by exercising some control over the apparatus used, the analyst can exert considerable influence over the actual contamination levels for a given operation. For example, Plexiglass and nylon sieve sets are available that greatly reduce contamination levels of metals compared with brass or stainless steel sieve sets.

Solid materials are usually more stable than liquids and usually exhibit little interaction with their containers, which are typically glass or polyethylene. As long as the sample is not abrasive, there is little likelihood of contamination from a glass container. N.B.S. Standard Reference Materials (S.R.M.s), such as bovine liver, pine needles or orchard leaves, are packaged in glass containers. However, stability is not something that can be presumed. For these particular S.R.Ms it was necessary to freeze-dry the samples and sterilize them by radiation for stability. In other cases it may be necessary to package under an inert gas or take extraordinary measures to keep the sample dry.

For the clinical or medical researcher, there is considerably more difficulty in obtaining a valid sample. Every medical instrument used must be considered in terms of its ability to contaminate the specimen. For example, a stainless steel scalpel blade can be expected to elevate nickel levels in tissue greatly. If nickel were an element of interest, an alternative blade fabricated from tungsten would be a more appropriate choice than a stainless steel blade. Obviously, clinical and certain other samples require refrigeration or freezing to prevent the deterioration of the sample. A sampling protocol for autopsy samples of human liver has been developed at N.B.S. (Harrison *et al.* 1981) in which these and other problem sources have been addressed.

In general, most sampling difficulties are at least partially soluble if the analyst recognizes the potential for problems in advance and acts accordingly. Where contamination is a problem, the degree of success in sampling will depend on how well the contamination can be controlled. There is an important philosophical distinction between control, which implies that there is still contamination but at a reduced level, and the elimination of contamination, which may be a physical impossibility. Contamination is under control when its influence is reduced to an insignificant level, i.e. the accuracy of the analysis is not affected by the contamination.

Liquid materials tend to be more homogeneous but they are not necessarily easier to sample. Liquids interact chemically with sampling apparatus and containers, whereas most solid

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sample–apparatus interactions result from abrasion. Water samples are frequently filtered through a 0.45 μm membrane filter to remove suspended and particulate matter. This presents an opportunity for the filter or the filter apparatus to contaminate the sample being filtered and even an opportunity for some sample analyte loss through physisorption or chemisorption on the filter or apparatus.

Sea water sampling is one of the most demanding of sampling tasks, both because many elemental concentrations are very low and because the sampling ship itself produces such a vast pool of contamination. Many different sea water samplers have been described in the literature, and a good review source on environmental sampling has been compiled by Maienthal & Becker (1976). The Teflon sea water sampler described by Patterson (1976) would have to be ranked as one of the most elaborate. For many applications at the so-called state of the art, the design of the sampling apparatus becomes as critical as the actual analytical measurement. Nothing that follows can be any better than the quality of the sample initially obtained.

Stabilization

The analyst's first task is to obtain a representative sample and then to maintain or preserve that sample until it is ready for analysis. Unfortunately, many samples are not chemically, physically or biologically stable as they are sampled, and need to be manipulated or stabilized to preserve elemental concentrations. These problems usually result in loss of the element sought. The techniques used for preservation must be considered after some study; however, some generalizations are possible.

Solid materials (e.g. soils or freeze-dried materials) frequently do not need refrigeration or other treatment and may be quite stable. Exactly how stable a material needs to be is a function of shelf life and intended use. Stability requirements for an S.R.M. with a shelf life of 5–10 years must be quite high. Conversely, a sample with a 10% annual concentration change may be more than stable enough if it is analysed within a matter of hours after sampling.

Samples destined for long-term storage have a potential for bacterial degradation, moisture loss or gain, CO_2 loss or gain and a host of other problems. Generally, reference materials or N.B.S. S.R.Ms have had these problems well researched and a shelf life will be specified if one is applicable. Even with a solid sample, the analyst should be concerned with the useful shelf life of the sample. This may even be a function of the element sought, as some organometallic compounds have considerable volatility and thus their concentration may change with time.

Liquid samples may suffer from either or both of two fates during storage. At trace concentrations, the first and most obvious is that of contamination from the container, and the second is from adsorption of the sample analyte on the container walls. The first problem is avoidable or at least minimized through the proper selection and cleaning of the storage vessel. Acidification of the sample is the measure usually employed to avoid or minimize the latter problem of sample loss. However, acidification also increases the rate of extraction of trace elements from the walls of the container, thus contaminating the sample. This means that even greater importance must be attached to the matter of container selection and cleaning. At N.B.S., water samples are routinely acidified to 0.5 M with nitric acid and have proved to be stable for most trace elements. Other researchers advocate different, usually higher, pH values, but a reasonable consensus seems to be that a pH of *ca.* 1 is adequate for most trace elements.

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Another technique that may be employed to stabilize samples is that of freezing. As temperatures are lowered, the activities of ions are reduced and interactions between sample and container are reduced. Certain samples, such as serum or tissue, require freezing or refrigeration to avoid the chemical and physical deterioration of the sample. Another related technique is that of freeze-drying or lyophilization. By removing most of the water from the sample and sterilizing by radiation, if necessary, it is possible to produce a more stable sample form that may require no refrigeration.

However, freeze-drying may cause the loss of many volatile elements such as mercury and thus should be used with caution. With a freeze-dried reference material the losses are immaterial since it is the concentration of trace elements in the freeze-dried material (not the original sample) that is certified. Even if it is not used as a stabilization technique, freeze-drying of aqueous samples may be a useful technique for sample preconcentration.

Sample storage and containers

These subjects are interrelated since any sample in storage must be contained. The best advice on sample storage is to avoid it as much as possible: minimize contact time with all containers. The length of storage, the type of container and its cleanliness, and the conditions of storage all affect the degree of sample contamination during storage. Zero levels of contamination are unlikely in the real world. Therefore the analyst must choose a level of effort in contamination avoidance that will produce acceptable results for the particular sample of interest. For example, a stabilized sample of waste water with high trace element levels will require a less scrupulously cleaned container than a stabilized estuarine water sample. Since contamination itself cannot be eliminated, any sampling programme must include blank samples designed to measure the level of contamination under conditions experienced by the samples.

Moody & Lindstrom (1977) have studied commercially available container materials used for trace element analysis, and their findings can be summarized briefly as follows. Among plastic materials, Teflon FEP bottles and apparatus are the cleanest of materials but also the most expensive. Teflon has the added advantage of a wide range of temperature tolerance and unexcelled resistance to chemical attack. This means that Teflon laboratory ware may be subjected to the most rigorous cleaning procedures without harm. Teflon containers also may be immersed in liquid nitrogen without cracking.

The other recommended container material is conventional polyethylene (CPE), which is comparable with Teflon in terms of trace element content. CPE materials have poor resistance to chemical attack and poor tolerance to high or low temperature storage. CPE bottles may be cleaned with relatively little effort and also are the least expensive commercially produced container. Because of its low resistance to chemical attack, CPE containers are not easily cleaned after use for a sample. Thus, CPE containers make an excellent choice for one-time, disposable use in sampling programmes.

For more permanent apparatus needs such as beakers, flasks or valves, Teflon is the more attractive choice despite its higher initial cost. Because it may be more thoroughly cleaned, Teflon presents fewer possibilities of cross-contamination between successive generations of samples. Furthermore, its greater tolerance of temperature extremes permits almost any sample chemistry except those that require fuming or boiling sulphuric acid.

T. J. Murphy (1976) summarized why glass is not a suitable material for most trace elemental

analysis. For trace organic analysis, the converse is true and plastic containers should be avoided. Apparatus fabricated from quartz may approach or even equal the contamination-free performance of Teflon. It is more expensive and fragile, but quartz may be used at much higher temperatures than Teflon. In addition, all plastic containers gradually lose water by permeation through the walls. Annual rates of loss may exceed 3 % (Moody & Lindstrom 1977), whereas it is easily possible to control such losses in quartz to 0.01 % annually. The recommended steps for cleaning of plastic containers according to Moody & Lindstrom (1976) are summarized in table 1.

TABLE 1. SUGGESTED METHOD FOR CLEANING PLASTIC CONTAINERS

1. fill with 1+1 HCl (analytical grade)
2. allow to stand for 1 week at room temperature (80 °C for Teflon)
3. empty and rinse with distilled water
4. fill with 1+1 HNO_3 (analytical grade)
5. allow to stand for 1 week at room temperature (80 °C for Teflon)
6. empty and rinse with distilled water
7. fill with purest available distilled water
8. allow to stand for several weeks or until needed, changing water periodically to ensure continued cleaning
9. rinse with purest water and allow to dry in a particle-free and fume-free environment

Since temperature controls rates of diffusion or leach rates, this variable has the potential to affect the amount of contamination received by the sample in storage. Under the most demanding requirements, a sample may be frozen or even stored at liquid nitrogen temperatures. Low-temperature storage has been in use at N.B.S. for a pilot study of a National Environmental Specimen Bank (Harrison *et al.* 1981). To date, sections of human liver have been obtained, packaged and frozen under the most scrupulously clean conditions. Repeated analyses over the next several years will permit a more conclusive evaluation of this method of sample preservation. Preliminary data indicates that trace element concentrations have been stabilized.

Liquid samples may be extremely difficult to stabilize. However, our experience at N.B.S. has been that stable solutions of up to 20 elements may be kept for periods of 5 years and more. All of these solutions were acidified to 0.5 M in nitric acid and concentrations were between 1 ng ml^{-1} and 1 μg ml^{-1}. The implication is that any solution of trace elements that is free from particulates, organics or complex anionic species can probably be stabilized in a similar manner. There is no general technique for water stabilization and a trial and error process may be necessary for many samples.

Any type of sample may have a tendency to gain or lose water, CO_2 or other volatiles such as organometallics over a period of time. Some of these problems such as water loss may be avoided by proper packaging, e.g. placing the sample container in a bag made of an impermeable material. Other problems may be detected and corrections made for by taring the container and reweighing the sample before and after storage.

THE ROLE OF PURIFIED REAGENTS

In the 10 years since the sub-boiling distillation of reagent acids from quartz stills was described by Kuehner *et al.* (1972), and a similar process in a two-bottle Teflon still was described by Mattinson (1972), these distillation techniques have become a major part of the newer methods of analysis. Table 2 reproduces the results obtained by Kuehner *et al.* for nitric acid

compared with commercially available high-purity acid and reagent acid. Similar types of improvements have been shown for all of the mineral acids and HF, which is distilled from an all-Teflon still.

In the intervening years, a number of papers have been published that contain one or more modifications to the basic techniques in the first two pioneering papers. Although no substantial improvements have been made in the quality of the acids produced, the use of these acids has gained widespread acceptance due to the overwhelming improvement in the reagent blank as a result of using purified reagents.

TABLE 2. TYPICAL IMPURITY CONCENTRATIONS IN NITRIC ACID (NANOGRAMS PER GRAM)

element	acid from sub-boiling still	A.C.S. reagent grade acid	commercial high purity
Pb	0.02	0.2	0.3
Tl	—	0.2	—
Ba	0.01	8	—
Te	0.01	0.1	—
Sn	0.01	0.1	1
In	0.01	—	—
Cd	0.01	0.1	0.2
Ag	0.1	0.03	0.1
Sr	0.01	2	—
Se	0.09	0.2	—
Zn	0.04	4	8
Cu	0.04	20	4
Ni	0.05	20	3
Fe	0.3	24	55
Cr	0.05	6	130
C	0.2	30	30
K	0.2	10	11
Mg	0.1	13	—
Na	1	80	—
total	**2.3**	**220**	**240**

To achieve a 0.5 M concentration of nitric acid requires a significant addition of nitric acid to a water sample. By using reagent acid, blanks for Cu, Ni and Fe approach 1 ng ml^{-1} just from this acidification step. Purified reagents can reduce this contribution to about 0.002 ng ml^{-1}. When similar comparisons are made for sample dissolution (wet ashing) and ion exchange separations, total system blanks may be reduced from microgram to nanogram levels or less, depending on the exact size of the sample and the type of sample chemistry required.

Preparing and using purified reagents has a direct beneficial effect upon the practical lower limit of analysis. When combined with adequately clean containers and apparatus and with similar control of environmental contamination, it is not unreasonable to expect a 100-fold to 1000-fold improvement in the analytical blank and a commensurate lowering of the analytical detection limit. For most laboratories that consume relatively small amounts of reagent, the two-bottle still represents the most practical method. The quartz stills are expensive but easily justified for a laboratory that consumes 1 l or more of purified acid per week.

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Apparatus and chemistry

Just as important as the selection of the material for a sample container is the choice of material for other apparatus used in trace analysis. To avoid contamination from glass, commercially available apparatus manufactured from Teflon or CPE may be substituted for almost familiar laboratory glassware. Sometimes the miniaturization or specialized design of an apparatus can be used to reduce sample contamination. Zief & Mitchell (1976) have reviewed many techniques for purification and contamination control.

Frequently, the selection of sample chemistry can largely determine the success of an analysis. For example, certain organic materials such as residual fuel oils require very careful, lengthy wet digestions that consume large amounts of perchloric and nitric acids, thus increasing the analytical blank. A sealed-tube technique using only nitric acid has been used at N.B.S. which is fast, may produce a lower blank for some elements and avoids the use of perchloric acid, which could be undesirable for certain analyses. Thus although most sample digestions may be carried out successfully in a Teflon beaker, there are alternatives such as the sealed tube or one of the commercially available Teflon bombs.

Separations are another area where an examination of available methods may produce a more efficient separation. Ion exchange is a useful technique by which many separations can be effected. For some samples such as sea water, a chelating resin (Kingston *et al.* 1978) has significant advantages in terms of speed and blank reduction. Even more classical chemical techniques such as precipitation may be employed to scavenge or co-precipitate a desired element from a solution (Mitchell 1981).

The chemist

So far, the chemist has been portrayed in a sympathetic manner, making decisions in the course of an analysis that can improve the result. The chemist can also have an unintentional deleterious effect upon an analysis. A habitual smoker is a poor candidate for a trace chemist for several reasons. An unintentional cough is one means of causing sample contamination. Flaking skin and even fibres from the clothes of a smoker will be higher in trace element levels due to contamination from cigarette ash and smoke.

Table 3. Lead leached from fingers by dilute HNO_3

(Two fingers dipped in 2 ml of 2% HNO_3 for 2 min.)

	lead found
High reading	13.1
Low reading	0.8
Average of 16 individuals	3.1

Certain medications may cause an increased rate of perspiration, thereby increasing the salt concentration on the skin. Soaps or even shampoos may leave a residue of metals such as zinc. Upon careful analysis the analyst himself may be seen to be the source of many forms of contamination harmful to the sample. Gloves, protective outer clothing and good personal and work habits are among the preventative measures that are possible. Murphy (1976) reported the lead levels extracted by a brief acid rinse of the fingers of a number of trace analysts at

N.B.S. The results, shown in table 3, are both surprisingly high and variable. Gloves (with no talc) would minimize the potential for contamination from hands. The effect of long hair and beards should also not be overlooked. Appropriate head covers are available. With care and foresight most of the problems associated with the chemist may be minimized.

Environmental control

Although this subject is the last category to be discussed, it is one of the most important for trace analysis. The air we breathe is burdened with much particulate matter that ranges from very few 100 μm particles per cubic metre to exponentially increasing numbers of particles of smaller sizes. Small particles have little mass and a short half-life, whereas large particles are too heavy to remain suspended in the air for long. Most particulate contamination of analytical significance is in the 1–10 μm size category.

To aid in visualizing the significance of these numbers, the normal laboratory air at N.B.S. averages about 30 000 000 particles integrated between 0.5 and 100 μm per cubic metre of air. By most standards the N.B.S. is considered to be in a relatively clean suburban area and much higher particulate counts are obtained in more urban or industrialized conditions (Maienthal & Becker 1976). Much of this particulate matter comes from automobile exhaust and lead blanks of *ca.* 0.5 μg m^{-3} of air have been found at N.B.S. (Maienthal & Taylor 1970). The exact contamination levels would be a function of the time of exposure to the laboratory air.

Slightly more than 10 years ago, N.B.S. completed a clean room specifically designed for trace element chemistry for samples received from the Lunar Apollo program. This clean laboratory design has been refined and reproduced by a large number of laboratories in the United States. All of the techniques described in this paper are routinely used at N.B.S. and many other leading trace element laboratories in the U.S.A. and Europe. A complete clean laboratory may not be necessary for the best work, but it does greatly simplify work conditions and is highly recommended to those who can afford it.

The best clean rooms in the United States are specified to meet or exceed Federal Standard 209b (1973) class 100, which basically requires a maximum particle count of 100 above 0.3 μm particle size (the practical particle size limit for optical instrumentation) per cubic foot of air. Coincidentally, 0.3 μm is the point of minimum efficiency for the Hepa (high efficiency particulate) filter, which is the heart of a clean room. Although the clean air technology has existed since World War II, practical laboratory applications in chemistry have appeared only during the last decade.

Figure 1 details the air flow characteristics of the N.B.S. design compared with two conventional designs. A major problem in a working laboratory has always been fume control and the corrosion of the laboratory itself (causing sample contamination). Clean rooms of older design could not maintain class 100 air quality with the corrosion and rusting due to chemical fumes. Thus, a major thrust of N.B.S. efforts has been toward the elimination of metal fixtures and their replacement with wood, glass plastic or other non-metallic substances, which do not produce particles. Where metals are required, for structural reasons, aluminum metal has been used and coated with a polyurethane paint for corrosion resistance.

The clean lab with its integral class 100 laminar air flow Teflon fume cupboards (hoods) has obvious applications in the chemical dissolution and processing of a sample. The laboratories at N.B.S. actually measure closer to 5 particles per cubic foot (*ca.* 125 per cubic metre) and

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therefore have been quite effective at isolating the sample from contamination. The design has also been effective in minimizing contamination directly from the chemist. Analytical blank reduction has been achieved primarily through the use of the clean laboratory for chemically processing the samples, the use of purified reagents for sample chemistry, and clean laboratory apparatus fabricated from Teflon or polyethylene.

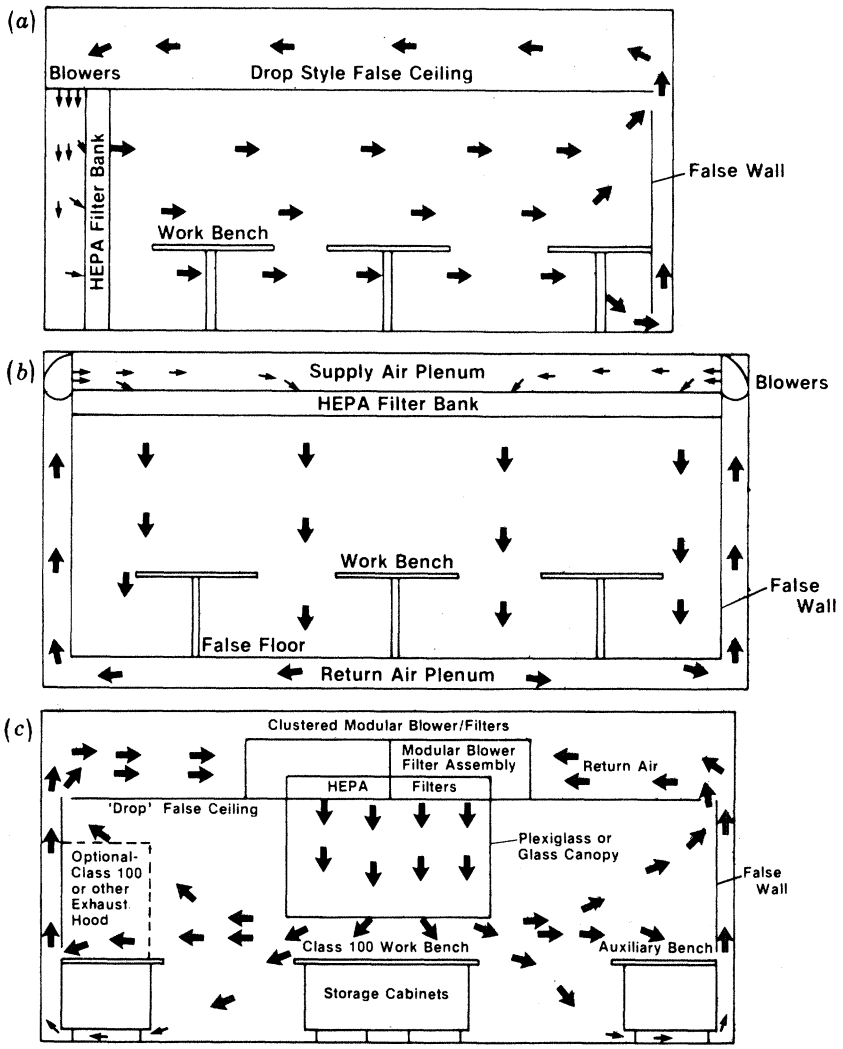

FIGURE 1. (*a*) Horizontal flow clean room; (*b*) vertical flow clean room; (*c*) N.B.S. clean laboratory.

However, a lesser known use of clean air technology has been in the sampling operation itself. Even in an otherwise pristine environment, the air itself may seriously contaminate the sampling apparatus and the sample. For the most demanding field operations, a portable class 100 clean air shroud can protect sensitive samples from contamination. Similar small, portable clean air work benches are available for laboratory use. A special laboratory has been built at N.B.S. for the Environmental Specimen Bank that uses both activated charcoal-treated and HEPA-filtered air to achieve low levels of contamination for organic and inorganic materials in the ambient laboratory air. Of course, not all samples will require such rigorous handling

criteria but it should be appreciated that the technology is there when it is needed. Lastly, HEPA filters can only remove particulates, and not gases such as tetraethyl lead. Clean air flows protect samples and not the chemist: beware of hazards.

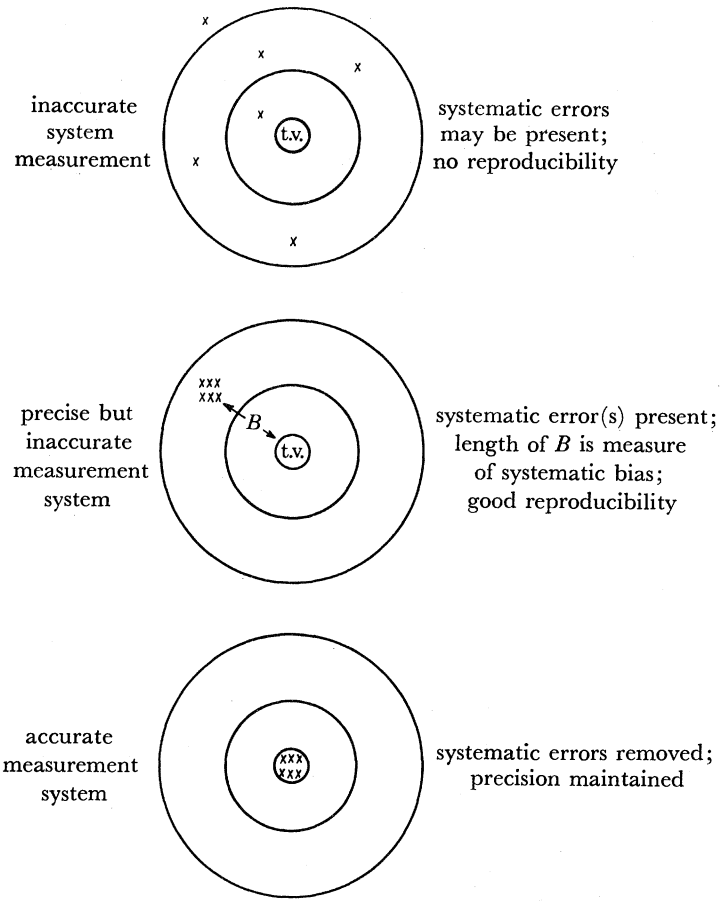

FIGURE 2. Formal definition of a Standard Reference Material; t.v., true value.

THE USE OF APPROPRIATE REFERENCE MATERIALS

The object of trace analysis, or any analytical scheme, is to be both precise and accurate. Figure 2 summarizes the usual results in real life. Results may be imprecise and inaccurate at the same time. Results may also be very precise and yet still inaccurate. The researcher working with a new sample usually does not know the 'true' answer and thus is likely to estimate accuracy on the basis of analytical precision. If you can appreciate this phenomenon happening concurrently in many laboratories you can begin to understand the confusion that results from the reporting of inaccurate data.

One function of N.B.S. and other standards organizations is to promote the technology for accurate measurements. By using an N.B.S. S.R.M. or other certified standard, the researcher is able to analyse and duplicate all of the analytical errors that could have happened to the experimental sample. If the certified values of the S.R.M. cannot be reproduced under the same conditions of analysis as the sample, there is every reason to believe that an analytical problem exists in the sample analysis as well.

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Standards do not exist for every type of material, but those currently available are very wide in scope and can be used for many different samples. For example, N.B.S. has a number of botanical standards including citrus leaves, orchard leaves, pine needles, and others. The more closely the standard matches the matrix composition of the sample, the more valid the use of the S.R.M. as a control will be. Catalogues of reference materials from N.B.S. and other organizations such as The Central Bureau for Nuclear Measurements, The Bureau of Analyzed Samples, Bundesanstalt fur Materialprüfung, and Bureau National de Metrologie are usually available upon request.

TABLE 4. INFLUENCE OF LEAD BLANK REDUCTION ON T.E.G.† ASSAYS

	lead found μg
initial analysis	330 ± 250
T.E.G. analysis with selected acids	260 ± 200
T.E.G. analysis in class 100 hood	20 ± 8
T.E.G. analysis with special acids in clean lab (lunar sample conditions)	2 ± 1

† T.E.G., Trace Elements in Glass, S.R.Ms 610–619.

TABLE 5. INFLUENCE OF SILVER BLANK REDUCTION ON T.E.G. ASSAYS

	lead found μg
initial analysis	970 ± 500
T.E.G. analysis with class 100 hoods	207 ± 200
T.E.G. analysis with special acids in clean lab	3 ± 2

SUMMARY

A prime objective of this paper has been to demonstrate that there are numerous influences upon an analysis other than the instrument. As presented, certain of these influences can be modified, controlled or understood well enough to minimize any influence upon the analysis. The danger in a very general review of this type is that it will be perceived as too academic and not relevant. Tables 4 and 5 contain data tables designed to demonstrate that very dramatic changes in the apparent analysis may result when contamination controls are introduced. In these cases, both sets of data were 'best efforts' results obtained at a time before and after the construction of the first N.B.S. clean lab and pure reagents lab.

Although these examples were deliberately chosen, it is important to realize that the earlier analyses were inaccurate by more than one order of magnitude, and in each case the uncertainties were almost entirely due to a high analytical blank. With analysis contamination under control, it is possible to approach the 'true' value and to be able to discern influences on the result due to sampling, inhomogeneity, ageing, etc. Frequent reference has been made to activities at N.B.S., not with the intention of slighting other institutions but for the sake of convenience. Most of the research areas covered have been the subject of considerable research at N.B.S. and while space does not permit enumerating their contributions, I should like to acknowledge that many others are responsible for the work described. In particular, the reader is urged to consult the authoritative paper on the analytical blank by Murphy (1976). Information on the Environmental Specimen Bank programme should be in the open literature in the near future; a summary of the project is currently available as U.S. E.P.A. report no. EPA-600/51-81-025, May 1981.

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