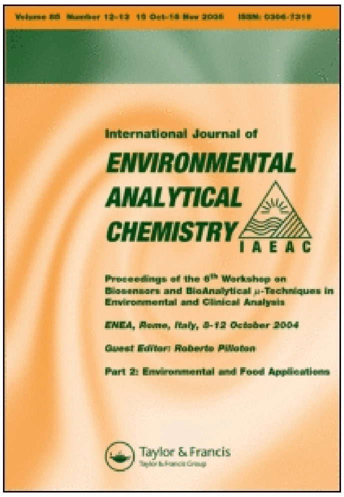

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Trace Analysis in Industrial Research

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To cite this Article Gallivan, J. B.(1974) 'Trace Analysis in Industrial Research', International Journal of Environmental Analytical Chemistry, 3: 3, 191 — 198
To link to this Article: DOI: 10.1080/03067317408071081
URL: http://dx.doi.org/10.1080/03067317408071081

Intern. J. Environ. Anal. Chem., 1974, Vol. 3, pp. 191–198
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Printed in Great Britain

Trace Analysis in Industrial Research†

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(*Received August 23, 1972*)

KEY WORDS: trace analysis, industrial methods, pollutants.

Public concern and legislative regulations governing environmental pollution have had a dramatic effect on chemists involved in industrial research. The need to establish both the presence and amounts of trace levels of pollutants in industrial products and wastes has become imperative. Since time and cost become important considerations in such analytical determinations, it is apparent that sensitive, rapid and reliable methods of trace analysis are required. Many experimental techniques have been employed to this end and active research programs exist to develop new techniques to make such analysis more efficient.

Techniques capable of determining many elements in a single examination of a sample are of particular interest. No single 'black box' approach is, or is likely to become, feasible for all species of interest. Nonetheless, certain multi-element approaches provide adequate information on some species and also provide important guidelines on the determination of other species by more specialized techniques. Problems encountered and progress achieved by the application of various spectroscopic, chromatographic, electrochemical and chemical methods to the trace analysis of industrial materials will be discussed.

INTRODUCTION

Trace analysis in a modern industrial research laboratory is important not only from an environmental but also from a production point of view. The number of conferences and publications on environmental pollution that have appeared in recent years, attest to the tremendous surge in public and

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†Presented at the Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Halifax, N.S., August 23–25, 1972.

private awareness of our environmental problems. Now that some of the problems facing us have been recognized, some concrete steps are being taken to ensure that further degradation of the environment does not occur. Government agencies, such as the Environmental Protection Agency (EPA) in the United States, have been established and are now able, with legislative approval, to set limits on the levels of many recognized pollutants in industrial products and effluents. Requests for this information have resulted in a very significant increase in the number of trace analytical determinations being made throughout the chemical industry.

In this era of transistors and semiconductors, phosphors and highly specific catalysts, trace constituents are frequently responsible for major deficiencies in product performance and process efficiency. To maintain and improve existing products and processes, and to assist in the search for new and better products, we often need a better understanding of fundamental phenomena. Frequently this means that our analytical determinations must be more sensitive and more reliable. Often the same methods of analysis can be applied to both environmental and production problems. The techniques involved may be quite sophisticated, the instrumentation expensive, and the personnel needed to operate the instrumentation and interpret the data are usually highly trained. All of these necessary ingredients for rapid, sensitive and reliable analytical determinations can be found in a modern industrial research laboratory. In this paper some efforts made in trying to co-ordinate trace analytical determinations at the Stamford laboratories will be discussed.

APPROACH INVOLVED

Whether the problem which confronts us is environmental or production-oriented, a project rather than a technique-oriented approach is used. Consequently, this paper will reflect this viewpoint. Of course, each scientist involved in a project and whose contribution is to make a particular analytical determination, has to be concerned with all the specifics of his or her technique and how these specifics apply to the problem being considered. For obvious reasons, the details of these individual techniques will not be presented here.

Since 'trace analysis' may have rather different meanings to different analysts, Pinta's[1] definition, which designates species present at concentrations below 0.1 to 0.01% in a given medium as 'trace components', is used in this paper. When guidelines exist which indicate the sensitivity, accuracy and precision required for a given determination, a major objective is to satisfy these requirements with a minimum expenditure of time and effort. For elemental determinations, the use of multi-element (survey) techniques are obvious as long as these basic requirements are satisfied. For species not detected, and those for which these requirements are not met by a survey technique, any number of specialized techniques are available for further analyses. The survey and more specialized techniques will be considered separately, with some emphasis given to our efforts in the former classification.

SURVEY TECHNIQUES

Commonly used elemental survey techniques that we have investigated include atomic emission spectrography (AES), X-ray fluorescence spectroscopy (X–RF), and neutron activation analysis (NAA). For many years we have used AES to identify the metals present in a sample and to estimate their concentrations, at least semi-quantitatively. After some general comments relating to the relative merits of the three survey techniques listed, our attempts to automate and improve the qualitative and quantitative reliability of spectrograpic analysis will be described very briefly.

In the last decade there have been significant advances in the analytical capabilities of X-ray fluorescence. Modern X–RF instrumentation is now capable of performing quite extensive elemental surveys. Our investigations have shown that these surveys are still not as inclusive as atomic emission, and sensitivities towards many elements, particularly those of very low atomic number, are not as impressive. NAA can provide an even more inclusive survey than atomic emission, but has relatively poor sensitivity for some of the most common and most important elements, such as iron and lead. NAA is most sensitive to some of the rarest of elements, including dysprosium and europium. Additionally, to achieve the highest sensitivities possible, very high neutron fluxes are required. This usually means that large reactors or accelerators are required and major capital expenditures are involved. It is our opinion therefore, that although there are advantages and disadvantages associated with all three survey techniques, that if one must choose, AES is the most flexible, rapid, and least costly.

In the past two years we have attempted to standardize our arc source atomic emission procedures and automate the plate-reading operation for trace analysis. The objective was to make the total operation less dependent on the talents and prejudices of the analyst and thus more flexible and quantitative. Many of the concepts involved in this operation are not original or unique. Others[2,3] have taken atomic emission spectra on photographic plates, scanned the plates on a densitometer and transmitted the information present to a computer. Suitable programs have been used to enable the computer to reduce the data and print out the results. The application to trace element surveys, for up to 66 elements, constitutes the uniqueness of our approach. The elements included in the survey are listed in Table I.

Included among the input data for the computer program for these analyses are the wavelengths of as many as seven standard lines per element, relative intensities of each of these lines based on calibrations with standards of known concentrations in a matrix buffered with spectrographic carbon, and a designated 'key line' for each element which must be located to verify an element's presence. Elements are identified by distances from reference (Hg) wavelength lines which are superimposed on the emission spectrum. Concentrations are determined by line densities, as compared to densities obtained from known concentrations of the same element.

TABLE I

Elements included in a computer programmed automated scan of atomic emission spectra recorded on photographic plates.

Ag	Ce	Ge	Mn	Pr	Sn	V
Al	Co	Hf	Mo	Pt	Sr	W
As	Cr	Hg	Na	Rb	Ta	Y
Au	Cu	In	Nb	Re	Tb	Yb
B	Dy	Ir	Nd	Rh	Te	Zn
Ba	Er	K	Ni	Ru	Th	Zr
Be	Eu	La	Os	Sb	Ti	
Bi	Fe	Li	P	Sc	Tl	
Ca	Ga	Lu	Pb	Si	Tm	
Cd	Gd	Mg	Pd	Sm	U	

Of those elements surveyed in a normal scan of the near-u.v. spectral region, detection limits range from ~0.1 ppm for Be to ~1000 ppm for K, when a standard 15-mg charge of the element in spectrographic carbon is used. These limits frequently can be extended downwards by three of four orders of magnitude for aqueous and organic samples, because of the ability to concentrate trace constituents by evaporation or dry ashing. A rapidly rotating log step sector disc and a log step filter are used during each exposure, so that for each sample burned three exposures, differing in intensity by the ratios 1:8:64, are available for scanning. With this flexibility, a significant range of line densities can be scanned and the most favorable for each element used in estimating concentrations. Inherent limitations in the photographic process, matrix effects (even with buffering by spectrographic carbon), and variable phenomena in the burning process itself, limit our claims on precision for general applicability to ±X2. For samples of the same general nature, where matrix effects can be eliminated, or reduced effectively, and an internal standard can be added to each sample, this precision can be improved considerably. There are still problems in the total operation which we are trying to correct.

A sampling of the format of a typical printout of the data as it is being collected is shown in Table II. Distances along the plate are converted to wavelengths, and when these wavelengths match those of standard lines (within limits which vary with the dispersion of the instrument, but are <0.5 Å throughout the spectrum) of programmed elements, they are assigned to these elements. The magnitude of the difference in wavelength between each assigned line and that of the standard line to which it corresponds, is likewise indicated. Line densities are integrated over the full width of a line, which means that with data points taken every 4 microns, 10 such data points would be counted in a typical line of ~40-micron width. The integrated areas are then compared to the corresponding areas of these same lines for known concentrations of the elements, and the calculated concentrations given in per cent terms. The format for the final printout of results is given in Table III. When more than four lines of an element are located a second concentration estimate, which does not include the lowest and highest values obtained, is given in parentheses.

TABLE II

Format of data printout for computer analyzed atomic emission spectrum

Distance (mm)	Area	Wave-length (Å)	Assigned element	Conc. (%)
0.00	0.24E−01	2478.93	C	
0.24	0.54E−01	2479.55		
2.09	0.56E−01	2484.22		
4.62	0.86E−01	2490.68		
6.90	0.12E−01	2496.54	B (.24)	0.148E−02
10.89	0.17E+00	2506.90	Si (.00)	0.512E−01

SPECIALIZED TECHNIQUES

Table IV lists some of the techniques employed regularly and some typical determinations associated with each of them. The challenge to the individual scientist in an industrial laboratory comes from the need to keep abreast of new developments in his field, to innovate whenever it is desirable, and to use his or her special talents to help solve the diverse problems which are encountered. The determination of a given species in water, in basic inorganic and organic chemicals, in dyes, pigments, drugs, and a variety of consumer products presents a broad spectrum of challenges. Frequently, several different methods of detection may have to be used, together or independently, to help solve a given problem.

TABLE III

Format of an emission spectroscopy report listing trace elements found in a commercial polymer

Element	No. of lines	Conc. (ppm)	
Al	(3)	8.86	
Cr	(7)	17.20	(16.90)
Fe	(7)	30.20	(26.80)
Mg	(5)	3.11	(1.98)
Mn	(6)	2.57	(2.74)
Mo	(3)	1.28	
Si	(7)	8.12	(8.78)
Sn	(4)	2.73	

TABLE IV

Specialized techniques frequently used in trace analytical determinations

Technique	Type of species determined
Absorption spectrophotometry (colorimetry)	As, Si, conjugated organics
Anodic stripping voltammetry	Cd, Cu, Pb
Atomic absorption spectroscopy	Flame Cr, Ni, Zn
	Flameless Hg
	Carbon rod Co, Mo
Fluorimetry	Se, aromatics
Gas chromatography	Organics (PCB's)
Ion specific electrodes	CN^-, F^-, NH_4^+
Microcoulometry	S, N

Some of these specific techniques, such as atomic absorption spectroscopy (AAS) and anodic stripping voltammetry (ASV), permit essentially simultaneous detection of several species. In this respect they may be considered more efficient than those techniques which are highly specific towards a single species for a given sample preparation. Frequently, techniques such as TLC and fluorescence spectroscopy are used in combination to achieve desired analytical results. The chromatographic separation of trace components from complex mixtures makes it possible to use the spectroscopic technique to identify and quantify these traces. The ability to separate and concentrate these minor constituents has enabled us to use infrared and n.m.r. spectroscopy neither of which is generally thought of as a trace probe, to determine the nature and amounts of species present at ppm levels in some samples. Multiple internal reflection techniques in infrared, and signal averaged n.m.r. spectra make sensitivity limits of this magnitude possible.

TABLE V

Format[a] for a trace species report on a commercial acid

Constituents		
Mercury	< 10 ppb	(Flameless AA)
Lead	0.05 ppm	(ASV)
Arsenic	0.07 ppm	(Spectrophotometric)
Cadmium	0.007 ppm	(ASV)
PCB's	< 1 ppm	(Phosphorimetric)
Phenol	< 0.01 ppm	(Spectrophotometric)
Cyanide	< 0.05 ppm	(Ion specific electrode)
Antimony	< 1.5 ppm	(AE spectrography)*
Beryllium	< 0.02 ppm	(AE spectrography)
Copper	0.07 ppm	(ASV)
Selenium	0.002 ppm	(Fluorimetry)
Zinc	0.1 ppm	(Atomic absorption)

[a]The other metals requested were determined by AES.

APPLICATIONS

As one example, the approach to providing the data necessary to answer a customer's inquiry as to the concentrations of certain species in a commercial acid is described. Typically, the sample is surveyed initially by AES to determine which of the listed elements are present. The approximate concentration of those elements observed is determined and maximum concentration estimates made for those elements listed, surveyed for, but not observed. For those elements for which this information is not adequate, and for those species listed which are not detected by AES, a number of the more directed analytical methods are used. A representative sample of a report listing techniques employed and the results obtained for one of Cyanamid's products is shown in Table V.

CONCLUSIONS

The products and effluents of the chemical industry present so many diverse analytical problems that any laboratory engaged in trace analysis must be flexible and innovative. Rapid communication, modern instrumentation, and the combined efforts of people with diverse backgrounds and talents, are all essential if these analytical determinations are to be efficient and complete.

Acknowledgment

The author is indebted to those members of the Scientific Services Department at Cyanamid's Stamford Laboratories who have contributed to our trace analysis program. In particular, J. P. Mohns, M. V. Norris, B. G. Roberts and R. C. Sampson have made very significant contributions to the program and to this paper.

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