

Atsushi Mizuike

Enrichment Techniques for Inorganic Trace Analysis

Chemical Laboratory Practice



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With 41 Figures and 49 Tables



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Chemical Laboratory Practice

Editors

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Preface

The significant role of trace elements present at the $\mu\text{g/g}$ (10^{-6} g/g), ng/g (10^{-9} g/g) and pg/g (10^{-12} g/g) levels in geological, biological, environmental and industrial materials has increasingly been recognized in science and technology. To detect and determine trace elements, we usually use modern optical, electrochemical and nuclear analytical techniques. Although most of them are highly sensitive and selective, preliminary enrichment techniques are required to extend the detection limits, improve precision and accuracy of analytical results, and to widen the scope of the determination techniques. About two decades ago, I wrote a chapter "Separations and Pre-concentrations" in "Trace Analysis: Physical Methods" edited by Prof. G.H. Morrison (Wiley-Interscience, New York, 1965). Since then, the progress in this field has been remarkable.

This monograph is intended as *a laboratory book directly applicable to the practice*, but is not a so-called "cookbook" which offers detailed laboratory instructions. I hope this book is useful for all analysts solving problems in inorganic trace analysis and appreciating the applicability and limitations of enrichment techniques combined with instrumental determination techniques.

In three introductory chapters, general aspects and control of contamination and loss are discussed. The following eight chapters deal with enrichment techniques based on volatilization, liquid-liquid extraction, selective dissolution, precipitation, electrochemical deposition and dissolution, sorption, ion exchange, liquid chromatography, flotation, freezing and zone melting. The final two chapters are devoted to special enrichment techniques used in trace analyses of natural waters and gaseous samples.

Finally, I wish to express my appreciation to my collaborators for their help in preparing this book, especially to Dr. Masataka Hiraide for literature survey, proofreading and valuable discussion, to Ms. Atsumi Kato for typing the manuscript, and to Mr. Tomokazu Tanaka for preparing the line drawings. Without their assistance, this book would never have appeared.

August 31, 1982
Nagoya, Japan

Atsushi Mizuike

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1 Introduction

Inorganic trace analysis or trace element analysis is defined as the *determination of trace elements at concentrations below about 100 $\mu\text{g/g}$ in inorganic and organic samples*. At present, trace elements even at the ng/g (10^{-9} g/g) and pg/g (10^{-12} g/g) levels can be determined with satisfactory accuracy and precision by using proper analytical techniques that, however, involve a number of difficult problems. The difficulties arise mainly from extremely low concentrations of trace elements in various matrices, not from absolute quantities of the trace elements.

1.1 Inorganic Trace Analysis in Science and Technology

Trace elements in terrestrial materials such as the atmosphere, ground, river, lake and sea waters, soils, minerals and rocks, and in cosmic materials such as meteorites, soils and rocks on the lunar surface have extensively been analyzed to obtain invaluable information in geochemical and cosmochemical studies. The role of trace elements in biological systems is very complicated. There are a number of essential, beneficial, harmful or toxic trace elements for plants and animals. Most of the essential trace elements whose deficiency gives rise to various diseases are toxic to plants and animals if present in excessive amounts, and the optimum concentration ranges are relatively narrow for some elements. Therefore, the atmosphere, drinking water, soils, plants, animal and human diets, and animal and human blood, urine and tissues are frequently analyzed for trace elements in biological, agricultural and medical sciences as well as in connection with environmental problems. Inorganic trace analysis is also very important in physical sciences and industry. The presence of trace impurities in materials such as high-purity metals, semiconductors and glasses has an important influence on electrical, magnetic, mechanical, nuclear and optical properties as well as on chemical resistivity. Impurities in raw materials such as petroleum and ores may cause troubles during manufacturing processes such as poisoning of catalysts and deterioration of production efficiency. Some trace elements in industrial effluent gases and waters are sources of environmental pollution. Other fields of application of inorganic trace analysis include criminology and archaeology.

To investigate the synergetic action and correlation of trace elements in high-purity materials, biological and environmental samples, etc., analytical results are necessary for the extreme variety of trace elements that may be present in the sample. If available, simultaneous multielement determination techniques are suitable for this

purpose, because time, labor, samples and reagents required for the analysis are minimized. Information on chemical forms as well as distribution of a trace element in the sample is also frequently required. As an example, the determination of the chemical forms of trace heavy metals in natural waters gives useful information in studies of geochemistry, environmental problems, biological effects of trace elements, and water treatment.

1.2 The Role of Enrichment Techniques in Inorganic Trace Analysis

The general scheme of inorganic trace analysis is shown in Fig. 1. To ensure sufficient precision and accuracy of analytical results in inorganic trace analysis, great care must be taken to minimize loss of the desired trace elements (trace elements to be determined) and contamination from external sources during the whole analytical process from the sample collection through the determination [1]. In addition, interferences from unexpected trace inorganic and organic substances coexisting in the sample may cause biases in analytical results. These problems generally become critical for trace elements at the concentration levels below $1 \mu\text{g/g}$.

Because of the low concentrations and the small absolute amounts of the desired trace elements, *highly sensitive and selective determination techniques* listed in Table 1 are generally employed. The absolute and relative (concentration) detection limits (expressed in absolute amount and in concentration) as well as the selectivity of each technique vary greatly with elements, matrices, analytical instruments, reagents, and various experimental conditions. Most of the techniques listed in Table 1 have absolute detection limits in nanogram (10^{-9} g) or picogram (10^{-12} g) ranges for many elements with adequate selectivity. In favorable cases, the absolute detection limits for some elements are in the femtogram (10^{-15} g) range or lower.

Direct applications of these determination techniques are, however, frequently impossible, difficult or undesirable,

(1) when the concentrations of the desired trace elements are below the relative detection limits of the determination technique,

(2) when substances which interfere with the determination exist in the sample,

(3) when the sample is highly toxic, radioactive, or expensive to be wasted,

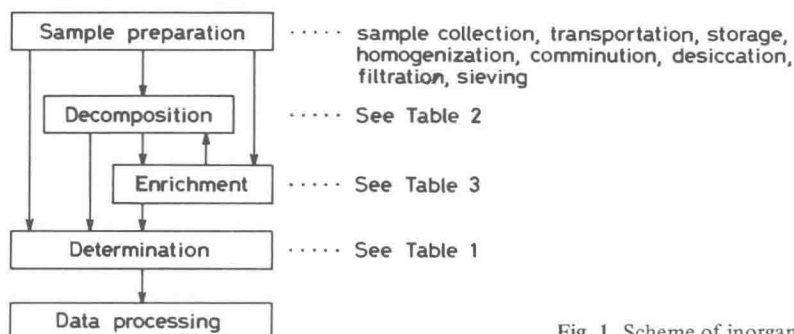


Fig. 1. Scheme of inorganic trace analysis

Table 1. Determination techniques used in inorganic trace analysis

Molecular absorption spectrometry – Ultraviolet, Visible, Infrared.
Luminescence spectrometry – Ultraviolet (Fluorometry), X-ray.
Photoacoustic spectrometry
Atomic absorption spectrometry – Flame, Electrothermal, Cold vapor.
Atomic fluorescence spectrometry
Optical emission spectrometry – Flame, DC arc, Spark, ICP, Microwave plasma.
X-ray spectrometry – Fluorescence, Electron probe, Particle-induced.
Mass spectrometry – Spark source, Ion probe, Isotope dilution.
Activation analysis – Neutron, Charged particle, Photon.
Isotope dilution-substoichiometric method
Polarography – DC, AC, Linear sweep, Square-wave, Pulse.
Stripping voltammetry – Anodic, Cathodic.
Electrochemical titrimetric methods
Ion-selective electrode potentiometry
Gas analytical methods
Gas chromatography
Liquid chromatography
Catalytic methods

(4) when the desired trace elements are not homogeneously distributed in the sample,

(5) when suitable standard samples required for the calibration are not available, and

(6) when the chemical or physical states of the sample are not suitable for the direct determination.

Decomposition (destruction) of the sample [2–4] and/or enrichment (preconcentration) of the desired trace elements prior to the determination can overcome these difficulties, extend the absolute and relative detection limits, improve the precision and accuracy of analytical results, and widen the scope of the determination techniques. The outlines of these two steps are tabulated in Tables 2 and 3. Sometimes, both steps are unified, e.g. in dry oxidation (ashing) of organic samples.

Table 2. Decomposition techniques used in inorganic trace analysis

For inorganic solids

Dissolution in mineral acids, organic acids, alkali hydroxide solutions, etc.

Fusion or sintering with alkali carbonates and hydroxides, sodium peroxide, alkali disulfates, etc.

Decomposition with reactive gases such as oxygen, chlorine and hydrogen fluoride.

Anodic dissolution (electrolytic dissolution)

For organic samples

Dry oxidation (dry ashing) in air, oxygen or oxygen plasmas.

Wet oxidation (wet ashing) with mineral acids.

Oxidative fusion with alkali nitrates.

Table 3. Enrichment techniques used in inorganic trace analysis

Sample state	Separated substances	Techniques
1. Solid or molten	Particles*	Manual selection under the microscope. Sieving. Magnetic separation. Heavy liquid separation. Flotation.
	Constituents	Selective dissolution. Electrolytic dissolution. Sublimation. Extraction of gases in metals at high temperatures. Dry oxidation of organic samples. Zone melting. Fire assay.
2. Solution	Particles*	Filtration. Centrifugation. Flotation.
	Solutes	Precipitation. Electrodeposition. Adsorption. Molecular sieving. Ion exchange. Liquid-liquid extraction. Volatilization. Flotation. Freezing. Electrophoresis. Dialysis. Ultrafiltration. Ultracentrifugation.
3. Gas	Particles*	Filtration. Impaction. Sedimentation. Centrifugation.
	Constituents	Thermal precipitation. Electrostatic precipitation. Absorption. Adsorption. Condensation. Permeation.

* Particle diameter > ca. 0.5 μm

Enrichment is a process in which the ratio of the amount of a desired trace element to that of the original matrix is increased. Foreign substances are frequently introduced into the sample during the enrichment process. Thus the original matrix is converted into a new matrix which is more suitable for the determination; e.g. a 1-g solid metal sample into a 1.0-ml aqueous solution containing the desired trace element and a microgram quantity of the original matrix. Therefore, enrichment does not necessarily mean increase in the concentration of the desired trace element. Enrichment is attained by the use of various separation techniques based on physical, physico-chemical and chemical principles. Most of frequently used enrichment techniques including liquid-liquid extraction and ion exchange depend on distribution of the elements of interest between two phases followed by physical separation of both phases.

2 General Aspects of Enrichment Techniques

Important considerations in selecting and evaluating enrichment techniques are discussed in this chapter:

trace recovery,
enrichment factor,
contamination,
simplicity and rapidity,
and sample size.

2.1 Trace Recovery

The trace recovery (R_T) or the yield of the desired trace element is defined as

$$R_T = Q_T/Q_T^0 \times 100 (\%) \quad (1)$$

where Q_T^0 and Q_T are the quantities of the desired trace element before and after the enrichment, respectively, the latter being corrected for contamination.

The trace recovery is usually less than 100%, because loss of the desired trace element may occur during the decomposition and enrichment steps by evaporation, incomplete decomposition, incomplete separation, careless manipulation, and strong adsorption on the walls of the containers and other apparatus used. The trace recovery varies with concentration levels. In general, the lower the concentration, the more the danger of losses. The well-known anomalous behavior of trace elements at extremely low concentrations [5, 6] is frequently responsible for the loss. Trace recoveries of greater than 95%, or 90% at least, are required in most inorganic trace analyses. If sufficiently reproducible, lower trace recoveries can be used for the correction of analytical results. Much lower and even variable recoveries are permissible in isotope dilution analysis and radiochemical separations using isotopic carriers.

The recovery and loss of the trace element are best investigated by the *radioactive tracer technique*. A radioactive isotope of the trace element is added as tracer to the sample before the enrichment step, and its behavior is followed by rapid, sensitive and selective radioactivity measurements. The great advantage of this technique is that the recovery and loss are measured independently of contamination hazards. Although both the isotope and the radiation effects are generally negligible, it must be kept in mind that the radioactive isotope added is in the same chemical form as the

desired trace element. A limitation of the applicability of this technique exists in the difficulty of introducing tracers into solid samples for investigating the recovery and loss of trace elements during decomposition of solid samples as well as separations by volatilization and solvent extraction of trace elements from solid samples. Radioactivation (irradiation of solid samples with thermal neutrons) or synthesis of solid samples containing radioactive isotopes is sometimes useful.

When suitable radioactive isotopes are not available, *standard samples*, i.e. certified standards, analyzed samples or synthetic samples, are used for measuring trace recoveries. The method of standard addition is also useful. In all these cases, however, contamination should be negligible or reproducible and accurately determinable.

2.2 Enrichment Factor

The enrichment factor (F) or preconcentration coefficient of the trace element is defined as

$$F = \frac{Q_T/Q_M}{Q_T^0/Q_M^0} = \frac{R_T}{R_M} \quad (2)$$

where Q_M^0 and Q_M are the quantities of the matrix before and after the enrichment, respectively, and R_M is the yield of the matrix. The enrichment factor required depends on the concentration level of the desired trace element in the sample as well as on the determination techniques used. Enrichment factors greater than 10^5 are sometimes required, which can be easily attained by some enrichment techniques with satisfactory trace recoveries. In most inorganic trace analyses, however, enrichment factors of 10^2 to 10^4 are sufficient, because modern instrumental determination techniques have low detection limits and adequate selectivity. Enrichment factors can be increased by using proper multistage separations without appreciable loss of the desired trace element. The ratio of the concentration of the desired trace element after the enrichment to that of the original sample is virtually the same as the enrichment factor when the matrix does not change, but is not when the matrix conversion occurs during the enrichment.

2.3 Contamination

During the enrichment and related steps, contaminants containing the desired trace elements may be introduced into the sample from external sources including the laboratory atmosphere, the reagents, containers and other apparatus used, and the analyst performing the analysis, which give positive biases in analytical results. Airborne dust particles can adsorb the desired trace elements in the sample solution and cause negative biases. Some extern-

ally introduced foreign inorganic or organic substances may interfere with the determination and cause positive or negative biases in analytical results.

In inorganic trace analysis, a "blank run" is usually carried out in parallel with the analysis under the same conditions but without the sample, and the resulting "blank value" is subtracted from the analytical value. This method, however, is quite unsatisfactory to correct the effects of contamination because of the following three reasons:

(1) Most kinds of contamination are not reproducible. For example, the degree of airborne contamination varies with time and place. The contamination due to surface erosion of containers depends greatly on the history of the containers, the cleaning procedures used, as well as the solution composition in which the analysis and the blank run differ.

(2) When the standard deviation of the analytical value A is σ_A and that of the blank value B is σ_B , the relative standard deviation of the corrected value $(A - B)$ is $100 \sqrt{\sigma_A^2 + \sigma_B^2} / (A - B) \%$. When $A \gg B$ and $\sigma_A \gg \sigma_B$, the relative standard deviation becomes $100\sigma_A / A\%$, which is usually sufficiently small. As the difference between A and B decreases, the relative standard deviation increases, and when $A \approx B$ and $\sigma_A \approx \sigma_B$, it is $141\sigma_A / (A - B)\%$, which is quite large. Therefore, even when the contamination is reproducible, the corrected value is imprecise for an analytical value having a corresponding blank value of the same order of magnitude.

(3) Loss of the desired trace elements may occur simultaneously with contamination during the analysis and the blank run in different manners. Accidentally, loss and contamination may cancel each other and an uncorrected analytical value with an apparent trace recovery of about 100% or a blank value of nearly zero may be obtained, although appreciable loss and contamination exist.

The degree of contamination is estimated more reliably by analyzing standard samples or by carrying out the analysis with various sample weights and extrapolating the analytical values to the sample weight zero. These methods, however, are still unsatisfactory.

Therefore, minimization of contamination is essential to attain accurate analytical results in inorganic trace analyses. If possible, the degree of contamination should be less than one tenth of an analytical value. It is desirable to investigate loss (by the radioactive tracer technique) and contamination in each analytical step separately, and correction is made according to these results, instead of simple subtraction of the overall blank value from the analytical value. Differentiation of contamination from various sources is possible under proper experimental conditions: e.g. contamination due to a reagent is estimated separately by analyzing a large amount of the reagent under the conditions where contamination due to the atmosphere and containers is negligible.

2.4 Simplicity and Rapidity

Most analysts may think enrichment techniques take much skill, labor and time. Therefore, enrichment techniques should be as simple, easy and rapid in operation as possible. Efforts to this goal are often also effective to minimize loss and con-

tamination. It must be kept in mind that sometimes combination of two or more simple enrichment techniques is superior to a single difficult enrichment technique as a whole. Simultaneous multielement enrichment techniques are preferable for simultaneous multielement determination techniques such as optical emission spectrometry and X-ray fluorescence spectrometry and also for rapid single-element (one-element-at-a-time) determination techniques such as atomic absorption spectrometry. Smooth connections with the preceding steps (sample preparation or decomposition) and the following steps (another enrichment or determination) are very important. Some enrichment techniques are unified with another analytical step; e.g. enrichment of particulate matter in air and natural water samples (with sample preparation), oxidation of organic samples and fire assay of ores (with decomposition), and carrier distillation in optical emission spectrometry (with determination).

2.5 Sample Size

The required sample size depends on the concentration levels of the desired trace elements as well as the absolute detection limits of the determination technique used. Ordinarily, solid samples of 0.1 to 10 g and liquid samples of 10 to 1000 ml are taken for the enrichment of trace elements at the ng/g or low $\mu\text{g/g}$ level. Much larger samples are sometimes used for trace elements at the pg/g or low ng/g level. Theoretically, it would be possible to determine infinitely low concentrations of trace elements by applying enrichment techniques to an infinitely large sample. In reality, *the lowest detectable concentration levels are limited by contamination, loss, and interferences from other trace constituents* present in the sample, and increasing the sample size becomes useless for extending the relative detection limit. In addition, manipulations for decomposition and enrichment become very difficult and inconveniently time-consuming when the sample size is extremely large.

Some kinds of samples, such as ultrahigh-purity metals and compounds, and other rare natural and artificial substances, are very expensive or available only in small quantities. Modern instrumental determination techniques with excellent absolute detection limits enable one to determine trace elements at the ng/g or low $\mu\text{g/g}$ level in milligram samples. Enrichment techniques operated on a microscale (microliter levels) are frequently very useful in the effective application of such determination techniques as optical emission spectrometry, spark source mass spectrometry, atomic absorption and fluorescence spectrometry by electrothermal atomization or by flow-injection techniques, and electron and ion microprobe techniques, where the maximum size of a solid or liquid sample is limited to the low microliter level or lower. Microscale operations have several advantages, i.e. economy in sample, high-purity reagents and time, as well as minimization of experimental wastes. Microscale operations, however, sometimes need more skill and caution than conventional ones to ensure the precision and accuracy of analytical results.

3 Control of Contamination and Loss

As discussed in the preceding chapter, contamination and loss are among the most difficult problems in inorganic trace analysis, especially when enrichment techniques are employed. Their control is essential to obtain precise and accurate analytical results.

3.1 Airborne Contamination

The outdoor atmosphere contains various kinds of liquid and solid particulates, aerosols and dusts, which include soil dusts, sea salt nuclei, volcanic ash, pollens, bacteria and others of natural origin, as well as fly ash, oil smoke, sulfuric acid mist, cement dust and others of industrial or man-made origin. These particulates intrude into conventional analytical laboratories. Fig. 2 shows approximate sizes of such particulates [7]. Table 4 tabulates examples of trace elements in particulates in the atmosphere of various districts.

Table 4. Trace elements in airborne particulates

Concentration level (ng/m ³ air)	East Chicago, Ind., U.S.A. (industrial) [8]	Niles, Mich., U.S.A. (rural) [8]	U.S.A. (urban, average) [9]	Osaka and Sakai, Japan (urban) [10]	South pole [11]
10 ⁴ –10 ⁵	Fe, S	S			
10 ³ –10 ⁴	Al, Ca, Cu, K, Mg, Zn	Al, Ca, Fe	Fe	Al, Ca, Cl, Fe, K, Na, Zn	
10 ² –10 ³	Cr, Mn, Na, Ti	Cu, K, Mg, Na, Ti, Zn	Mn, Pb, Zn	Mn, V	
10–10 ²	As, Br, Ce, Sb, V	Br, Mn	As, Cr, Cu, Ni, Sn, Ti, V	As, Ba, Br, Cd, Cr, Ni, Sb, Ti	
1–10	Ag, Co, Ga, Hg, La, Sc, Se, Th, W	As, Cr, Hg, La, Sb, Se, Se, V	Cd, Sb	Ag, Ce, Co, Cs, Hg, La, Rb, Se, Th, W	Mg, Na