Photometric Determination of Traces of Metals

General Aspects

Fourth Edition of Part I of
Colorimetric Determination of Traces of Metals

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FROM THE PREFACE TO THE FIRST EDITION

The colorimetric determination of traces of elements, especially of metals, has made great advances in recent years and it seemed to the writer that it would be useful to have available a collection of modern methods in this field of analysis. This book is the result of an attempt in this direction. It is not intended to be an encyclopaedia of methods for the colorimetric determination of small amounts of metals. The aim has been rather to present a limited number of methods which at the present time appear to be best suited for dealing with traces of metals. No one reagent is necessarily the best for the determination of an element in all kinds of samples or under all conditions, and consequently two or three methods are sometimes described in greater or less detail for a number of the metals. A few fluorimetric methods are included. The treatment is to a considerable extent based on the experience of the writer in testing or using various methods.

Anyone who surveys the methods of colorimetric trace analysis must experience a feeling of satisfaction arising from the many sensitive reactions available and, on the other hand, of something close to dismay at our imperfect knowledge of the application of these reactions. The effect of foreign elements on a particular color reaction is frequently poorly known and the prevention of the interference of foreign substances has, for the most part, been incompletely studied. Methods for the separation of traces are but poorly developed or even non-existent for many elements. The user of this book is likely to find many of his questions in this phase of trace analysis unanswered in the present treatment. It is to be hoped that the workers of the future will be willing to devote as much of their energies to this prosaic aspect of the subject as to the more inviting one of searching for new reagents.

PREFACE

As indicated on the title page, this book is a revision of Part I of *Colorimetric Determination of Traces of Metals* (1959), which deals with general aspects of inorganic photometric analysis (molecular absorptiometry and fluorimetry) and with metal separations. Since the late 1950s, thousands of papers germane to the subject matter of this volume have appeared. An exhaustive treatment of this mass of material might have led to the exhaustion of the reader—and certainly of the authors. An eclectic approach would seem to have advantages and that is what we have attempted in this revision. A sufficient number of references have been given to provide points of entry into the literature. One-third of the treatment is devoted to separations.

At this time we have not decided whether to revise Part II of *Colorimetric Determination of Traces of Metals.* We believe that the applied analyst will continue to find Part II of the third edition useful for information on the separation and determination of traces of individual metals.

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CHAPTER

1

TRACE ANALYSIS: ROLE OF PHOTOMETRIC METHODS

I. PRELIMINARY CONSIDERATIONS

Trace analysis (quantitative) may reasonably be defined as the determination of constituents making up less than 0.01% of a solid sample.[1] Obviously, there is no need for, nor can there be, a sharp boundary between trace and nontrace constituents. The lower limit of a trace constituent is zero, but practically the lower limit is set by the sensitivity of available analytical methods and, in general, is pushed downward with the progress of analysis. In this book, the trace constituents considered are inorganic, and quantities usually refer to the elements.

In Fig. 1-1, the relative constituent content of a sample is subdivided logarithmically along the Y-axis, with major (100–1%) and minor (1–0.01%) constituent classes included.[2] Along the X-axis in this figure, the sample weight classes are designated. Samples weighing more than 0.1 g may be called macro; those in the range 0.1 to 0.01 g, meso

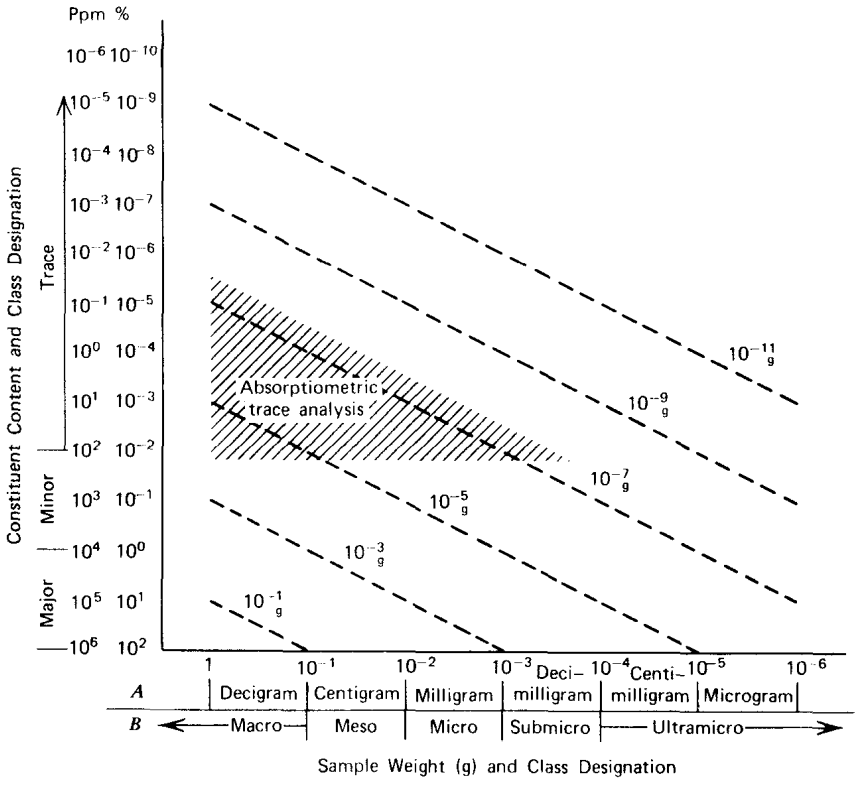

Fig. 1-1. Classification of analytical methods on the basis of sample size and constituent content. Major constituents make up 100–1% of a sample; minor constituents, 1–0.01%; and trace constituents, $< 0.01\%$ (< 100 ppm). The trace range is not subdivided into named classes, but these can be designated numerically, for example, 1–100 ppm, or as $-\log$ (concentration) = p (concentration). Sample-size classes can be named according to *A* or *B*, or designated numerically, for example, 10^{-2}–10^{-3} g. *Macro* and *meso* will generally be understood, but there is no agreement as to the naming or the range of the classes here called micro, submicro, and ultramicro. The slanting dashed lines indicate constituent quantities in grams. The constituent content–sample weight field of molecular absorptiometric methods is indicated. The approximate lower absolute limit of solution absorptiometric methods (spectrophotometry) in terms of constituent weight is based on the use of the more sensitive color reactions (0.001–0.003 μg of element detectable instrumentally in a column of solution of 1 cm^2 cross section). This weight is taken to be ten times the limit of detection. The volume of solution is assumed to be 5 ml contained in a 5 cm cell (or 10 ml in a 10 cm cell). This diagram is based on Fig. 1 in Sandell, *Colorimetric Determination of Traces of Metals*, 3rd ed., 1959.

("semimicro"); and those below 0.01 g may be subdivided as follows:

10^{-2}–10^{-3} g	micro (or milligram samples)
10^{-3}–10^{-4} g	submicro (or decimilligram samples)
$<10^{-4}$ g	ultramicro

(The naming of the latter classes is rather arbitrary and there is no general agreement on these designations.)

The diagonal lines in Fig. 1-1 indicate absolute amounts of constituents (in grams) as a function of the relative content of constituent and the sample size (= weight). Depending on the sensitivity of the method and the constituent content, the sample size in a trace determination may vary from macro to ultramicro. Ordinarily in trace analysis, the sample size does not exceed 1–10 g (often not above 1 g), but occasionally much larger samples are taken. For easily handled materials such as water or ice, samples in the kilogram or ton range may be used.

The essential feature of a trace analysis is not so much the determination of a minute quantity of a constituent, as it is the determination of such a quantity in the presence of overwhelming quantities of other substances that may seriously affect the reaction of the trace constituent.

II. METHODS OF ELEMENTAL TRACE ANALYSIS

Our purpose in this section is not to treat the principles of the various types of methods applied in inorganic trace analysis. The reader is assumed to be familiar with them in a general way.[3] We consider instead the general sensitivity, precision, accuracy, and selectivity of common trace methods. The treatment is not intended to be detailed or comprehensive, but it may serve as a survey of possibilities, allow some comparisons to be made among the various methods, and permit the reader to draw some conclusions regarding the capabilities of solution absorptiometric and fluorimetric methods in trace analysis.

With a few exceptions, the classical stoichiometric (gravimetric and titrimetric) methods are not used in trace analysis, chiefly because they lack sensitivity. Titrimetric methods are applied occasionally in the upper trace range. The determination of gold and other precious metals by cupellation, in which the metal bead is finally weighed to 0.01 mg, is almost the only important application of a gravimetric method in trace analysis. The method used by Haber to determine gold in sea water involved microscopic measurement of the metal bead to obtain its mass. A similar method was applied by Stock to determine mercury in various materials. These micrometric methods are now rarely if ever used.

The required sensitivity for trace determinations can be obtained by

using physical or physicochemical methods, in which manifestations of energy provide the basis of measurement. These methods are indirect in the sense that the emission or absorption of radiation or transformation of energy must be related in some way to the mass or concentration of the species that are being determined. The establishment of these relations almost invariably requires calibration, with the use of standards of known content of the constituent in question. For some types of methods, solutions of pure metals can be used. For others, solid standards of similar matrix composition are needed or are desirable. It is difficult to prepare such standards synthetically, and it may be necessary to use standards analyzed by another method; obviously, such methods have serious shortcomings as far as accuracy is concerned.

As a class, physical methods tend to be selective and may be rapid. When applied to trace constituents, they need not, as a rule, give results with errors less than a few percent—and such accuracy is not always readily attained in real analysis. Some physical methods—neutron activation, X-ray fluorescence, and flame or arc spectrography, for example—are more physical than others such as solution spectrophotometry and fluorimetry or electrochemical methods, which involve chemical reactions. The latter methods are best described as physicochemical.

We consider first the two types of methods that are the subject of this book, solution absorptiometry and solution fluorimetry, which for the want of a better term are here included under the term "photometric methods."

A. ABSORPTIOMETRY (SPECTROPHOTOMETRY) IN SOLUTION

Methods in this class are based on the absorption of radiation in the visible and UV (rarely the near infrared) portion of the electromagnetic spectrum by species in solution. The solutions are almost always aqueous or organic–solvent (rarely a melt), and the absorbing species are molecules or ions (hardly ever atoms).[4] The absorbing species are usually (and preferably) in true solution but may be solids in suspension or in a thin layer. The term "solution absorption spectrophotometry," while not entirely exact or all-inclusive, characterizes these methods fairly well, but is cumbrous. "Molecular (ionic) absorptiometry" conveys the meaning and distinguishes this type of method from atomic absorption. When, in this book, we refer to absorptiometry, we shall mean measurement of the absorption by species in solution, usually with a narrow band of wavelengths in the visible or the UV range. "Spectrophotometry" is another designation, which though not sufficiently restrictive, is usually

understood to mean the methods considered here. The older term "colorimetry" does not accurately describe these methods because nowadays absorption is frequently measured in the UV as well as in the visible range, but analytical chemists will understand this term as referring to methods used to determine the concentrations of dissolved constituents by developing light-absorbing reaction products by chemical reaction followed by spectrophotometric (usually absorptiometric but also reflectance) measurement or comparison. Most absorptiometric reagents in use today form colored products with the metals to be determined. At times the use of "colorimetry" may be advantageous or necessary, as when attention is called to absorption in the visible range.

Color comparisons based on the use of such reagents as ammonia (for copper), thiocyanate (for ferric iron and cobalt), and stannous chloride (for gold) provided the earliest physicochemical trace determinations in the nineteenth century. The development of organic chemistry over the last hundred years or so has led to the discovery and synthesis of many reagents giving colored (and some fluorescent) chelates and ion-association complexes with metals, which have been put to use in analysis. This has been followed by a more or less systematic search (by synthesis) for new sensitive and selective organic reagents. The commercial availability of photoelectric spectrophotometers before the middle of the present century allowed accurate determinations of both metals and nonmetals to be made with the aid of such reactions.

In the last 25 yr or so, new physical methods (p. 10–21) have been developed (emission spectrography was in use earlier) that have revolutionized trace analysis. Absorptiometric analysis is not as important as formerly. However, it still has a useful, even valuable, role to play in trace analysis, especially in the upper range of trace analysis.

Lower Limits. The lowest solution concentration, c_{min}, at which an element is detectable absorptiometrically is given by the relation:

$$c_{min} = \frac{A_{min}}{ab}$$

in which

A_{min} = smallest detectable absorbance ($\log I_0/I$).

a = absorptivity at some specified wavelength λ

= absorbance produced by a unit weight of element present as the absorbing species in a column of solution of unit cross sectional area (convenient units are $cm^2/\mu g$ or cm^2/ng).

b = light (radiation) path in centimeters.

(The assumption is made that A is rectilinearly proportional to b and c, so that a is constant; this is usually true in practice.)

a is typically 0.1–1 $cm^2/\mu g$ for the color reactions used in inorganic trace analysis. A_{min} depends on a number of factors, particularly on the absorptiometer used, but 0.001 is a good average value. We then have

$$c_{min} = \frac{0.001}{ab}$$

It is convenient to replace a by $1/(1000\mathscr{S})$, where $\mathscr{S}$ is the sensitivity index of the reaction, defined as the number of micrograms of the element, converted to the absorbing species, in a column of solution of 1 cm^2 cross section giving an absorbance of 0.001:

$$(c_{min})_{\mu g/ml} = (c_{min})_{ppm} = \frac{\mathscr{S}}{b}$$

Values of $\mathscr{S}$ for many color reactions are available[5] or can be calculated from molar absorptivities ϵ if the reaction runs to completion, or from apparent molar absorptivities if it does not. For the most sensitive color reactions, $\mathscr{S} = 0.002\ \mu g/cm^2$ on the average. Reactions having $\mathscr{S} = 0.002$–0.003 are available for at least 20 metals (Al, Sb, As, Be, Bi, Cd, Cr, Co, Cu, Ga, Ge, Au, Fe, Pb, Mg, Hg, Pd, Pt, Ru, Tl, and Zn). Very few reactions have $\mathscr{S} < 0.001$. It may be said then that with a 1 cm cell ($b = 1$) the lowest average c_{min} is ~0.002 ppm.

The lowest content of an element in a (solid) sample detectable absorptiometrically by a reaction of known $\mathscr{S}$ can be specified if the assumption is made that not more than 5 ml of solution is needed for the absorption measurement, the light path is 5 cm, and the sample size is 1 g. A final volume of 5 ml is quite realistic for most metal trace determinations, because a liquid–liquid extraction is, or can be, made that brings the colored or absorbing species into this relatively small volume, or other concentration methods can be used, although less conveniently. If the final volume is 10 ml, the light path should be 10 cm. Although there is no maximum sample size[6] when an isolation (concentration) procedure is used, it is convenient to limit the (solid) sample to ~1 g. A sample of this size is handled without much difficulty, even if a fusion procedure, as of a silicate with sodium carbonate, is needed to decompose the material. On the same basis as before, the minimal detectable element content in the sample then is $\sim(1 \times 0.002)$ or ~0.002 ppm. Now suppose that the limit of detection represents approximately the standard deviation in the determination of a trace constituent in its lowest range and that a relative standard deviation of 10% is acceptable in this range. The content of constituent in the sample should then be $\sim 100/10 \times 0.002 \sim 0.02$ ppm. Of course, it is possible that the standard deviation of the method is not

determined solely by the instrumental random deviation, here equated with the sensitivity. On the whole, in using colorimetric methods one would prefer to apply them to samples containing >0.1 ppm of constituent.

Generally, solutions giving an absorbance of ~0.4 provide the optimum precision if a transmittance scale of 100 divisions ($I_0 = 100$) can be read to 0.2 division (±0.2% I, absolute). (See Chapter 4.) Accordingly, under the conditions assumed (1 g sample, 5 ml final volume, 5 cm cell, $\mathscr{S} = 0.002$), no increase in photometric precision is to be expected above $0.4/0.001 \times 0.002 = 0.8$, or say 1 ppm of constituent. Therefore, if the constituent content is ~10 ppm, the sample size can be reduced to ~0.1 g, or if it is 100 ppm, it can be reduced to 0.01 g, and so on, for maximal photometric precision. With a 1 cm cell (5 ml volume), these weights would be multiplied by 5. Actually, in practical trace analysis, it is by no means necessary to strive for maximal photometric precision in all determinations, and, other factors remaining the same, smaller samples than indicated will often serve.

Precision and Accuracy. This topic is considered in Chapter 4, but some general statements are required in the present context. The random error in the measurement of absorbance, alluded to in the previous section, is only one of a number of errors afflicting absorptiometric determinations. There also may be random (indeterminate) errors in the color development step of the analysis. But determinate errors may be more important than indeterminate errors, and may be more difficult to evaluate. Absorptiometric analysis, like all other methods of analysis, is subject to positive and negative interferences. Hardly any metal color reaction is so selective that the possible reaction of other metals to give colored or absorbing species cannot occur. Negative interferences are of lesser importance. By adjustment of the hydrogen-ion concentration, use of differential complex formation or oxidation-reduction, it is often possible to eliminate or reduce the interference of foreign elements. But sooner or later such measures fail, especially in trace analysis, where the ratio of foreign elements to the element being determined is unfavorably large. Separations are then required to remove interfering elements and leave the desired element, preferably in a small volume of solution. Errors of two types can arise in separations: The recovery of the element in question may be incomplete and foreign elements may not be completely removed.

If blanks are large, precision may be impaired and determination limits may be raised.

Another source of error is in sampling. Because of heterogeneity the sample taken may not accurately represent the mass from which it is

derived. This error is likely to be smaller in absorptiometric analysis than in some other methods of trace analysis in which a smaller sample is used.

In the absence of interfering elements, the precision and accuracy of a method can be determined without any particular difficulty. When interfering elements are present, this will not be so easy, because both precision and accuracy, especially the latter, are likely to depend on the number and the amounts of these elements. The accuracy of a method can be tested by using synthetic samples containing known amounts of the element in question. This is laborious, and it may be done only by the originator or the modifier of a method. A simpler way involves analyzing a standard sample by the method in question, and comparing the result with the results that have been obtained by other methods of presumed accuracy. Comparison of results by different methods is a powerful means of detecting determinate errors, if the methods are so different that the same determinate errors are not likely to be present in all. It may thus be possible to establish the accuracy of an absorptiometric method for the determination of a particular element in a class of materials whose composition is represented by the standard sample. See Section III for comparisons of trace metal results given by different analytical methods.

Selectivity. The great majority of determination forms in molecular absorptiometry have broad absorption bands, so that attainment of selectivity by optical means (as in atomic absorption) is of limited value. Instead, chemical properties of reagents and constituents must be exploited. It may perhaps be doubted that any color reaction for an element, more particularly for a metal, is strictly specific, meaning that all other metals do not yield reaction products absorbing at or near the wavelength of maximum absorption of the element in question. Specificity is especially hard to attain in practice when the ratio of foreign elements to the given element is very large, say 10^5 or 10^6. But many color reactions are selective—only a few elements give a positive reaction similar to that of the element in question. The use of masking agents is of great help in improving selectivity. In practice, limited specificity is, as a rule, acceptable. That is, most methods described for the determination of a given element are suitable for certain classes of material, in which the amounts of foreign elements will not exceed certain limits. Very few methods to be found in the literature can be applied to a sample of any composition.

Sooner or later—usually quite soon in trace analysis—the analyst using absorptiometric methods (and other methods as well) is driven to separations in order to attain requisite specificity. A combination of a selective separation with a selective color reaction may give virtual specificity. Separations, as already mentioned, may result in appreciable loss of the desired element. Moreover, they lengthen the analysis. But separations

have one great advantage (if they are adequate): They make the determination independent of the composition of the sample. Matrix effects are virtually universal among physical trace methods for the elements, although the effects vary greatly from one method to another.

Some results are given later that allow judgments to be made concerning the accuracy and lower determination limits of absorptiometric methods in applied trace analysis.

B. FLUORIMETRY

Although the principles of fluorimetry and absorbance spectrophotometry are entirely different, it is convenient to consider fluorescence methods in conjunction with absorptiometric methods. Both are often included under "photometric methods." The apparative requirements are modest, and both methods are likely to require separations before they can be applied in trace analysis unless the samples are of the simplest type. Fluorescence methods are often more sensitive than the absorptiometric, sometimes by one or two orders of magnitude, but this is not always true. The sensitivity of a fluorescence method depends upon the intensity of the UV source, as well as other factors, and its objective expression is not as easy as for an absorptiometric method. Commonly, sensitivity is expressed in concentration terms, for example, the lowest concentration in ppm or $pp10^9$ (or even $pp10^{12}$) giving a detectable fluorescence under certain conditions, as with a specified instrument or solution volume. These concentrations are often in the $pp10^9$ range. For example, one commonly used fluorimeter in the USA allows a full-scale deflection (100 divisions) to be obtained with a 5×10^{-3}-ppm solution of quinine sulfate in water, and even a limit of a few $pp10^{12}$ has been claimed. A 10^{-4}-ppm solution of fluorescein gives a readily detectable fluorescence. With an esculin laser (to increase excitation intensity), the fluorescein detection limit is $\sim 2pp10^{12}$. With very few exceptions, organic reagents are used in inorganic fluorescence analysis, and the metal–organic compounds formed (often chelates) give sensitivities comparable to these. Bis-salicylalethylenediamine provides a sensitivity of 2×10^{-5} ppm for Mg, and 2-hydroxy-3-naphthoic acid a sensitivity of 2×10^{-3} ppm for Al and 2×10^{-4} ppm for Be in solution. Of course, not all fluorescence reactions are this sensitive.

Morin (Chapter 6B) is an example of a metal fluorescence reagent of demonstrated practical worth. It allows Be and Zr to be determined selectively in rather strongly basic and acid solutions, respectively. Instrumentally, 2×10^{-5} ppm of Be is detectable in solution, and visually, 4×10^{-4} ppm. Zirconium shows comparable sensitivities. With a 5-g

biosample (leaves), 0.01–0.02 ppm Be can be determined; the detection limit is 0.002 ppm or less. With a 0.02 g sample of silicate rock, 1 ppm Zr is detectable, and 10 ppm Zr should be determinable to ~10%.

Some of the fluorescent metal complexes (Al and Ga 8-hydroxyquinolates, for example) can be extracted into immiscible organic solvents, thus increasing the concentration sensitivity.

In principle, fluorimetric methods are more selective than absorptiometric. Fluorescent complexes are generally given by diamagnetic ions, not the paramagnetic, and thus the number of positively interfering elements is reduced. As in absorptiometry, the effect of interfering ions can be eliminated or reduced by differential complexing and occasionally by a change in oxidation state.

Fluorescence determinations are widely subject to negative (fluorescence diminishing) effects. On the whole, fluorescence methods are not as precise as absorptiometric methods, and they are not likely to be chosen in preference to them unless a definite superiority in sensitivity or selectivity can be demonstrated.

A fluorescence trace determination of great value is that of uranium. In a matrix of sodium fluoride or sodium fluoride-carbonate, U(VI) fluoresces an intense yellow-green. As little as 0.001 μg U in ~1 g of this flux can be determined with reasonable precision. The fluorescence is specific or almost so under suitable excitation conditions, but is subject to quenching by foreign substances, so that separations must often be made.

The price range of fluorimeters suitable for inorganic trace analysis is roughly \$500–2000 (1970). Measurements can be made with 0.5 ml volumes of solution, but unless extractions can be made, such small volumes are not likely to be useful in trace analysis. See Chapter 4 for further discussion.

As far as measurement is concerned, nephelometry is very similar to fluorimetry, the intensity of scattered light being measured instead of emitted radiation. A suspension of very slightly soluble substance is the basis of nephelometry. It is used very little in trace metal determinations. Absorptiometric and fluorimetric analysis is almost always superior in sensitivity and reproducibility.

C. ATOMIC ABSORPTION, ATOMIC FLUORESCENCE, AND FLAME EMISSION SPECTROPHOTOMETRY

Today (1977) more trace determinations are possibly made by atomic absorption spectrophotometry than by any other method. This popularity is due to the generally good sensitivity for many elements, the frequent lack of serious interferences, and commonly no need for separations

(except simple ones often made more for concentration than actual separation), rapidity, and satisfactory precision. For some elements, atomic fluorescence is more sensitive than atomic absorption. For still other elements, flame emission is more sensitive than either of these, though more susceptible to spectral interference ("... it is probably easier to obtain an erroneous result with a complex matrix in emission than with the other techniques."—Browner).

The detection limits of a number of metals by atomic absorption, fluorescence, and emission methods, all in flames, are given in Table 1-1. Customarily, the detection limits are stated in terms of solution concentration. What counts in applied analysis is the detection limit (and thence the determination limit) of an element in (usually) a solid sample. Assume that the solution sprayed into the flame is a 2% solution of the sample. Taking Be as an example, the detection limit by atomic absorption or fluorescence in the solid sample then is $(100/2) \times 2 \times 10^{-9} \times 10^{6} = 0.1$ ppm. Multiplying 0.1 by 10, we obtain 1 ppm Be as the approximate limit of *determination.* This is very satisfactory sensitivity, but it is no better than that provided by solution fluorimetry with morin as reagent. Some metals are not easily determined sensitively by atomic absorption with conventional equipment. Included among these are Th, Ce, rare earth elements, Hf, Zr, Nb, Ta, U, W, and Re. The sensitivity may be inadequate (as in geochemical analyses) for Sb, Ge, Ti, and Mo. (Almost all of these elements can be determined sensitively by solution absorptiometric methods.) On the other hand, the sensitivity is very high for Zn, Cd, and Mg. Flame emission is generally less sensitive than atomic absorption and fluorescence in flames, but for some elements (Group 6 in Table 1-1), it is more sensitive and to some extent is complementary to absorption and fluorescence. Extraction of a metal as a chelate into a suitable immiscible organic solvent is commonly used to increase the sensitivity in flame atomic absorption methods; extraction also has the advantage of separating the metal from other substances in the aqueous solution that could affect its determination.

The sensitivity of atomic absorption and fluorescence methods for some elements can be improved by substituting a graphite furnace or other nonflame atomizer for the flame. The atomic absorption detection limits in solution for a few metals are[7]:

Ag	0.0025 ng/ml
Au	0.08 ng/ml
Cd	0.001 ng/ml
Mg	0.1 ng/ml
Sb	0.2 ng/ml

TABLE 1-1
Detection Limits in Solution by Atomic Flame Methods[a]

		Detection Limit (ng/ml)		
	Element	Atomic Absorption	Atomic Fluorescence	Flame Emission
Group 1: Atomic absorption (AA) more sensitive than both atomic fluorescence AF and flame emission E	Be	2	10	1,000
	Hf	2,000	100,000	20,000
	Mg	0.1	1	5
	Mo	20	500	100
	Pd	20	40	50
	Sn	10	50	100
Group 2: (AA = E) > AF	Lu	700	3,000	1,000
	Rh	20	150	20
Group 3: (AA = AF) > E	As	100	100	10,000
	Fe	5	8	30
	Ni	2	3	20
	Pb	10	10	200
	Sb	40	30	600
Group 4: AA = AF = E	Cr	3	5	4
	Nb	1,000	1,500	1,000
Group 5: AF > (AA, E)	Ag	2	0.1	8
	Au	10	5	500
	Bi	25	5	2,000
	Cd	2	0.001	800
	Ce		500	10,000
	Co	10	5	30
	Cu	1	1	10
	Ge	200	100	400
	Hg	250	0.2	10,000
	Mn	2	1	5
	Tl	30	8	20
	Zn	1	0.02	10,000
Group 6: E > (AA, AF)	Al	20	100	5
	Ca	0.5	20	0.1
	Eu	20	20	0.5
	In	20	100	2
	Ru	70	500	20
	Sr	2	30	0.1
	V	4	70	10

[a] Selection of values from table given by R. F. Browner, *Analyst*, **99**, 617 (1974).