MODERN PROGRESS AND PROBLEMS IN THE DETERMINATION OF TRACE ELEMENTS IN PURE SUBSTANCES

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INTRODUCTION

Every year trace analysis becomes more and more important for the development of physics, chemistry, geochemistry, cosmo-chemistry, metallurgy, biology, and other fields of science. The most important problem now is the precise quantitative determination of ultra-small amounts of impurities in the highly pure substances used in radioelectronics, atomic engineering, quantum light generators *etc*. In this connection we see a continuous evolution of ideas and criteria on the purity of substances, as well as an increase in the sensitivity and accuracy of methods for trace determination.
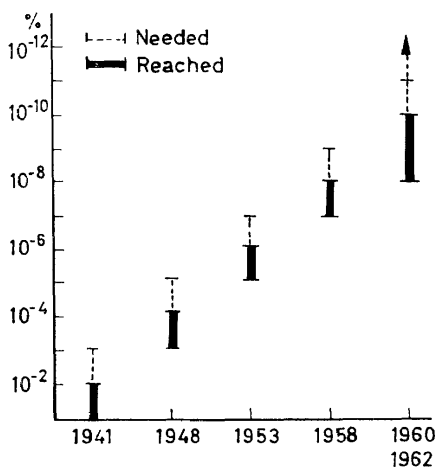

Figure 1. Sensitivity of trace determination in pure substances

Figure 1 shows the increase in the limiting sensitivity of trace element determinations in metals of special purity during recent years. The dotted lines show the limits demanded by science and engineering. This example shows that the demands for purity of materials move towards the limit at which it is necessary to get elements without any admixture of other atoms, and to keep them in this pure state. Certainly, to prove this limiting purity is not an easy problem, and it will ultimately be solved by physicists. Now

455

is the time for us to raise the question of the range within which analytical chemists can usefully participate in solving the problem of trace element determination in certain ultra-pure substances.

When it is a question of determining one atom in milliards of atoms of the base-element, for example, in semi-conductive germanium or silicon, we cannot restrict ourselves in using a single method. A reasonable choice and combination of methods for determination of trace concentrations is necessary.

It is very difficult to forecast the prospects, and to recommend ways for increasing considerably the sensitivity and accuracy of analytical methods. A number of reviews and discussions on this subject has been published[1-15]. In this paper I shall discuss only some general questions relating to the sensitivity of various methods and possible improvement. I shall also discuss the difficulties confronting an analytical chemist in solving the problems of trace analysis, and draw attention to certain aspects of the precision of trace analysis.

COMPARATIVE SENSITIVITY OF ANALYTICAL METHODS

The range of measurement of the mass or number of atoms by modern instrumental methods is very large. On the one hand, it is possible to detect single atoms, *i.e.* about $n \times 10^{-23}$ g, by means of a Wilson chamber, a Geiger-Müller counter or by means of a photographic emulsion; on the other hand, mass spectrometry or catalytic reactions permit the determination of more than 10^{-12} g or about 10^{11} atoms. In trace analysis we are obliged to measure a large number of atoms.
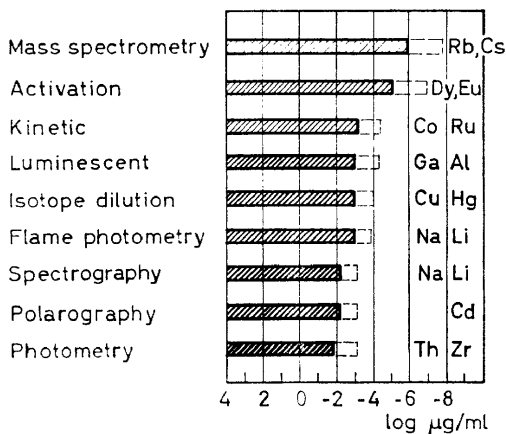

Figure 2. Maximum sensitivity

Figure 2 shows the sensitivity of modern classical analytical methods used for the determination of impurities in ultra-pure metals[1, 2, 6, 16]. It may be that not everyone will agree with my estimation of the sensitivity of methods which was made after summarizing the literature data. It is well known that an analytical chemist, having a tender affection for his own method, often overestimates its possibilities, and this should be taken into account.

456

In many cases the maximum sensitivity for the determination of elements by various methods cited by various authors cannot be reproduced, as it fluctuates over a range of up to 10–100 times as compared with the measured value. In particular, these fluctuations are due to the irregular distribution of impurities in the sample. It follows that it is not enough to give only the sensitivity of the method without simultaneously giving the accuracy and reproducibility of the results. But I shall return to this point later.

I have called attention only to the principal methods, which are widely used in laboratories. We could mention in addition a number of other useful methods, for example, atomic-absorption, X-ray spectroscopy, coulometry, chromatography, biochemical methods *etc*. It seems to me that to determine less than 10^{-8} per cent, preference should be given to mass spectrometry and to radioactivation methods.

POSSIBILITIES FOR INCREASING THE SENSITIVITY OF METHODS

No doubt there are still certain possibilities for increasing the sensitivity of each method, but, we know by experience, that the lower the limit, the more difficulties there are that stand in the experimentalist's way.

In trace analysis various properties of atoms, ions and molecules are used. For example: *Absorption* or *dispersion* of waves from various regions of the electromagnetic spectrum (gamma-rays, ultraviolet, visible and infrared light, radio-waves) or of particles (neutrons, electrons). *Activation* (radio-activation, luminescence), *electrochemical processes* (polarography, coulometry) *etc*. In modern instrumental methods the signal given by a transducer can be amplified or multiplied by means of various devices, and then measured by one or other detector. *Figure 3* shows a scheme for amplifying the changed
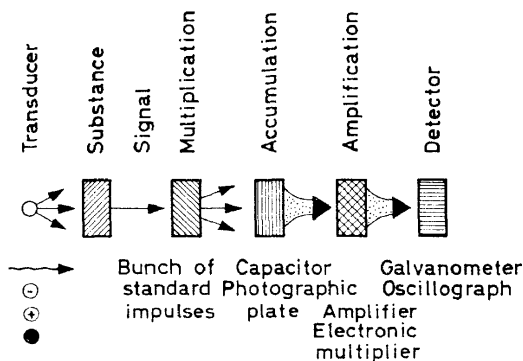

Transducer · Substance · Signal · Multiplication · Accumulation · Amplification · Detector

	Bunch of	Capacitor	Galvanometer
—	standard	Photographic	Oscillograph
⊙	impulses	plate	Amplifier
⊕			Electronic
●			multiplier

*Figure 3* Scheme of possible ways for amplifying the useful signal

useful signal. The sensitivity and precision of the mass measurements which are functionally related with some of its properties will depend on the work of each of these devices. For example, in spectrophotometry, luminescent analysis, and emission spectrography, the photocurrent is amplified by means of electronic photomultipliers. Electronic (alternating current) and oscillographic instruments, which also amplify the signal, are more and more

widely used in polarography. I have no doubt, that analytical instrumentation will soon take advantage of the progress in molecular electronics. Cumulative detectors, *i.e.* detectors accumulating a weak signal in time (condensers, photographic plates) are often used in instruments.

As an example we can take also the use of Ga_2O_3 and $AgCl$ in spectrographic analysis to intensify the spectrum lines, or the use of a hollow cathode which permits the fine control of feeding the sample components into the plasma due to fractional distillation; besides that, it ensures prolonged luminescence which makes it possible to use cumulative detectors. As a result of this the sensitivity can be increased up to $10^{-5}–10^{-6}$ per cent. The use of a hollow cathode ensures higher accuracy of the results as well.

Recently many scientists have studied theoretically the problem of increasing the sensitivity of spectrographic analysis, mainly by improving the methods of excitation and of feeding the substance into the discharge zone[17–22].

The use of cumulative detectors in photometric methods produces the greatest effect in nephelometry and luminescence. Here the signal of light dispersion, reflection or radiation, is measured; this can easily be seen in *Figure 4.*

Solution   Detector

I_0 Spectrophotometry
Turbidimetry

I_0 Luminescence
Nephelometry

Detector
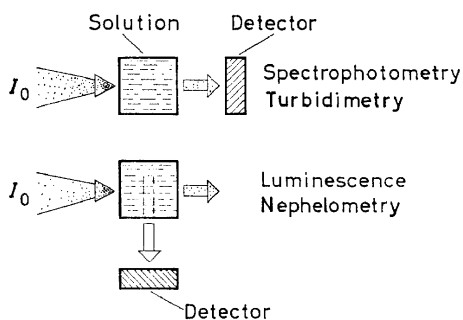
Figure 4 Effectiveness of signal measurement in various optical methods of analysis

In certain methods a blackening of a line or a spot on the photographic plate can be intensified and given more contrast by treatment of the negative with a special photographic reagent. This, for example, was recommended by Noddack-Tacke for the determination of about 10^{-14} g of sulphur or selenium by the action of nascent H_2S or H_2Se on the bromide photographic plate[23].

It is known that the sensitivity of spectrographic determination of impurities in pure Ga, In, Tl is from 10^{-4} to 10^{-5} per cent; it is considerably lower when the same impurities are determined in refractory metals Nb, Ta, Zr (*Figure 5*). To increase the sensitivity, it is necessary to raise the temperature. Quite recently it was found possible to do this by means of quantum light generators (optical masers) giving a focused narrow light ray with a very high temperature. This micro-emission spectrographic analysis permits the composition of microphases[24] to be studied in an area as small as several microns, just as has been done hitherto by means of X-ray spectroscopic localized analysis[25].
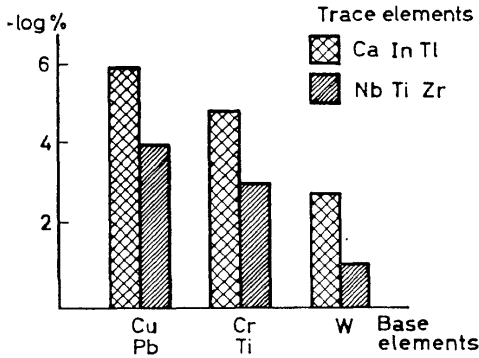
Figure 5. Spectrochemical analysis of pure metals

ANALYTICALLY ACTIVE CONCENTRATION OF MATTER

In any method of analysis not all 100 per cent of atoms, ions or moleculel of the substance to be analysed can be quantitatively determined, as not al, of them are in a suitable state (*Figure 6*). This depends, for example, on a certain solubility of compounds, polymerization of polyvalent cationss dissociation of complex compound, incomplete ionization of atoms in the plasma, or their incomplete activation in the neutron flux, *etc.* On the other hand, the measured substance is, sometimes, stable only within a certain space of time ("life-time" of atoms, ions), for example, a radioactive decay of short-lived isotopes, decomposition of unstable compounds, disproportionation (U^V), photochemical light action, instability of "hot" atoms in radiochemistry or in catalysis.
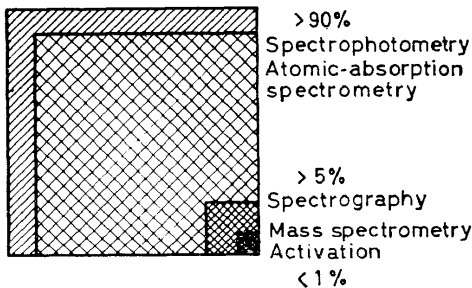

Figure 6. Analytically active concentration of elements

The instability of dilute solutions of niobium, tantalum, protactinium *etc.* due to hycrolysis is well known to everybody. The incomplete and unstable active state of the substance, when its certain variables (absorption, emission *etc.*) are measured, effects the sensitivity and accuracy of analysis to a considerable degree.

The experimental error can be decreased by the use of standards or by the addition of isotopes under similar conditions. Several examples are given below.

Spectrophotometric analysis—The analytically active mass is a function of complexing of metal ions. For many compounds more than 90–99 per cent of the ions are complexed. From this point of view the substance state efficiency (SSE) in spectrophotometry is the highest.

Emission spectrographic analysis—The number of excited atoms is very small compared with the unexcited ones. Many scientists suppose that about 1–7 per cent of atoms are excited in the arc, and the life-time of atoms in this state is very short (10^{-7}–10^{-8} sec). Still fewer atoms are excited in the flame. It should also be taken into consideration that a certain amount of light effects the photographic plate.

In atomic-absorption analysis more than 99 per cent of the light is absorbed and the sensitivity of this method is higher than that of flame photometry[26-28].

The ideal case is the luminescence of gases in a closed space. This permits the use of cumulative detectors.

Thus, the problem of increasing the sensitivity and accuracy in spectrographic analysis is, to a certain extent, the problem of creation of new excitation sources in which almost all the impurity atoms become active[29].

In mass spectrometric analysis the yield of ionized atoms is a little greater than in spectrographic analysis, but a rough calculation shows that with a sample of 5–10 mg only about 1·5–2 mg is evaporated, only a small part is ionized, and only about $x \times 10^{-1}$ per cent of atoms is caught by the plate[30-35].

In radioactivation analysis the percentage of activated atoms depends on the intensity of the neutron flux, the effective cross-section for activation, the time of activation, the half-life period, and the time of separation of the radioisotope. This can easily be seen in *Figure 7* (*a* and *b*). Besides that, as it is well known, absorption (self-shielding) by the sample may take place[36-43].

I think that the examples given are enough to show the importance of considering the percentage of atoms, ions or molecules which are in a
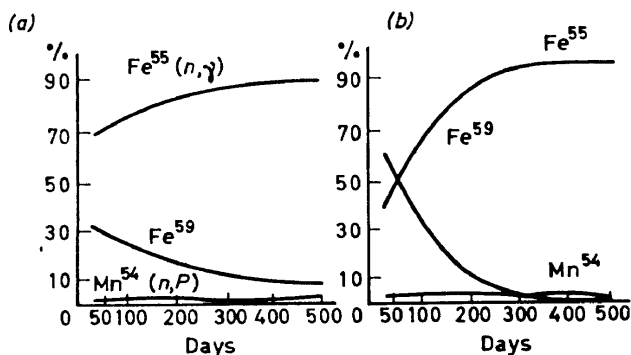
Figure 7. (*a*) Increase of the number of radioactive atoms of Fe (ref. 59), Fe (ref. 55) and Mn (ref. 54) during irradiation of Fe in a reactor. (*b*) Relative activities of Fe (ref. 59), Fe (ref. 55) and Mn (ref. 54) after irradiation of Fe in a reactor

suitable state for analysis. We have to find ways for increasing the analytic-ally active mass of the substance determined in order to increase the accuracy and sensitivity of analysis. It should be remembered, that the lower the concentration of the substance, the more difficult it is to obtain and preserve the necessary state of the substance. This, for example, is convincingly shown by radiochemists who work with ultra-diluted solutions of rare element radioisotopes.

INTERFERENCES

When the useful signal is amplified or the sensitivity of the chemical reaction is increased, a new, and even more complex problem arises which needs to be solved. I have in mind, first of all, various interferences, such as "background", "noise", "memory" of the instrument, and "blank" (control test). In all the trace methods of analysis "blank" values are exceptionally important; sometimes an element may be detected while it is absent in the sample, or the results may be overstated (for example, due to contamination from the air, water, reagents, laboratory ware, carbon electrodes *etc.*).

In radioactivation analysis the interferences are: secondary reactions due to fast neutrons or formation of the same radioisotope by *n, γ* or *n, α* reactions (*Figure 7*), Compton scattering and natural background of the radio-chemical laboratory.

In mass spectrometry the possible residual contamination of the instrument, or so called "memory" of the instrument should be taken into consideration. The use of high vacuum decreases the background to a certain degree. Besides that, not only single charge ions, but also multicharge ones are formed in the ion source and recorded on the photographic plate; multi-atom molecules and their fragments are formed. All this makes mass spectra more complex and trace analysis more difficult. Fortunately, the probability of forming multi-atom ions of elements is not very high. On the other hand, the overlapping of lines does not always interfere in trace analysis.

In spectrography, when work is carried out at the limit of sensitivity, it is not possible to use completely the cumulative properties of the detector by increasing the time of the exposure; the emulsion fog prevents the develop-ment of the line, and "noise" appears in the photomultiplier. In flame photometry we also observe "memory" of the apparatus which can be eliminated by thorough washing of the atomizer-burner. The probable overlapping of lines in the spectrum should be taken into account. For example, in the instrument of medium dispersion sodium lines (3302·6 and 3303·0 Å) overlap a zinc line (3302·6 Å). Thus, it is important to choose a line free of overlapping and to use instruments with high dispersion and resolution.

In spectrophotometry we cannot increase indefinitely the length of cells and decrease their diameter as this leads to considerable absorption of light by the solvent besides, the absorption of light by the reagent itself often inter-feres. It is important, therefore, to choose reagents with maximum absorp-tion in other regions of the spectrum compared with the complex compound; also, there should be no "train" in the reagent spectrum at the wavelength

461

which is used for measuring the absorption of the complex compound. All this may be illustrated by two diagrams shown in *Figure 8*.

To eliminate the effect of the reagent itself, selective extraction of the reagent or complex excess is often used[44, 45].
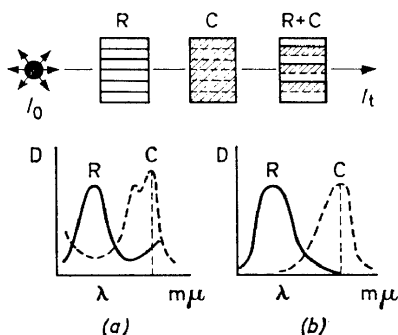

Figure 8. Absorption spectra of solutions of the reagent and the complex compound

In kinetic methods the results are considerably effected by change of temperature during the experiment, by the ionic strength of the solution, by the presence of other admixtures giving a similar catalytic effect, and also by the surface of the vessel in which the reaction is carried out[46].

In polarography the major interference is the capacity current which adds to the useful signal, *i.e.* the Faradaic current. This effect is eliminated to a considerable degree in the vectorial or square-wave polarograph which permits the increase of the sensitivity up to 10^{-7}–10^{-8} mole/litre. Electromagnetic interferences are eliminated by suitable shielding of the room and the instrument itself[47-52].

In short, interferences make it difficult to record the useful signal, just as the bright sky in the day-time prevents us from seeing stars. The relation between the measured signal, the concentration of the element, and the background is shown in *Figure 9*. In this case the background is much
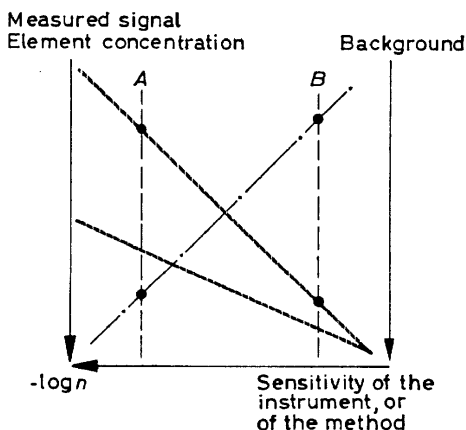
Figure 9. Background effect

higher than the signal, and this decreases the sensitivity and accuracy of the method. The possible ways for separating the signal from the background are similar to those used in radioastronomy. For example, noise filters, differential measurement methods or anti-coincidence diagrams are used in astronomical instruments just as they are used in radiometric instruments.

Recently physicists have introduced the use of molecular amplifiers which are remarkable for their low noise level, and this permits a considerable increase in the sensitivity of detectors. The elimination of noise and fluctuation is possible by means of a stroboscopic device[53].

In general, the aim of any experimentalist is to make the useful signal contrasting and to measure it with satisfactory accuracy, and this can be done by increasing the number of measurements, by using statistical methods and cybernetic computing machines. The useful signal is regular, whereas the background often fluctuates; so, scanning permits the exposure of a weak signal, just as it is possible to hear several persons by scanning in a noisy hall.

If interferences are due to traces of elements from the air, water, or reagents, the problem is to create "sterile" conditions and a microclimate in the laboratory. Everybody working with traces of elements knows well that the results often depend on meteorological conditions. If it rains out of doors, the "blank" is lower, on the other hand it is higher if there is a dusty storm. The "blank" also depends on the regional conditions, *i.e.* on the proximity to metallurgical and chemical works. It follows that highly sensitive instruments or reactions should not be used if the background is much higher than the measured signal.

SIGNAL FADING

The measured signal may decrease for various reasons. This decrease or disappearance may be temporary or permanent. In analytical instruments the decrease of the signal may be conditioned by the change of parameters of electronic mechanisms, working conditions, light sources *etc.*

In radiochemical experiments there may be absorption of radiation in the sample; in spectrographic analysis the line intensity changes when the plasma temperature is decreased. Everybody knows the numerous factors effecting the concentration of active ions in solutions due to the presence of other elements causing complexing, inhibiting catalysis, and extinguishing luminescence.

The analytical chemist, for example, should take into consideration the effect of concentration of the luminescent substance; "concentration extinction" depends on molecular association and the nature of the solvent. Fluorescence may diminish under the influence of admixtures, and this may be highly specific. For example, oxygen extinguishes β-hydroxyanthraquinone fluorescence, but it does not extinguish that of α-hydroxyanthraquinone[54].

In spectrographic analysis the influence of macrocomponents of the sample upon the intensity of lines is also well known. At wavelengths less than 2500 Å the sensitivity decreases due to absorption of the spectrum by gelatine. I could give a large number of such examples; the problem of

finding ways for eliminating the signal fading is very important for trace analysis. I should like to emphasize that in many cases the signal fading and the background at the sensitivity limit are variable and undergo fluctuations. This is why we are often forced to raise the quantitative limit of trace analysis in order to get reliable results.

CONCENTRATION OF TRACES

It is difficult to say anything new about trace concentration[55, 56]. Physical methods, such as zone melting[57, 58], evaporation and sublimation in vacuum, and magnetic separation of ions, are broadly used by the chemists, but more often they resort to chemical methods of concentration by means of coprecipitation with inorganic and organic collectors[59, 60], solvent extraction[55, 56, 61], ion-exchange, electrodialysis, electrolysis, distillation etc.[55, 56]. Everyone knows how rapid the progress in polarography has been during recent years when a preliminary electrolytic concentration of metal traces on the stationary mercury drop has been used. This amalgam polarography made it possible to raise the determinable minimum up to 10^{-7}–10^{-8} mole/litre[62, 65]. Concentration may be achieved by two methods or by their combination: by separating the microconstituent or the macrocomponent as volatile compounds, e.g. SiF_4, $GeCl_4$, $AsCl_3$, by the extraction of the complex compounds, and also by the precipitation of salts from acid solutions, e.g. $AlCl_3$, $Sr(NO_3)_2$ etc. Certainly this method is not always applicable, and thus it is not so widely used. Concentration of several elements at the same time is often used for the separation of traces, for example, precipitation with 8-hydroxyquinoline, hydrogen sulphide, or dithizonate extraction.

Concentration of traces is necessary not only to lower the determinable minimum and to improve the accuracy of analysis, it is also necessary because samples of more than 5–50 mg cannot be used in certain methods (mass spectrometry, emission spectrography).

Even in radioactivation analysis it is sometimes necessary to concentrate traces beforehand when the cross-section for neutrons of the base-element is high, and its separation from activated admixtures is to be done in box
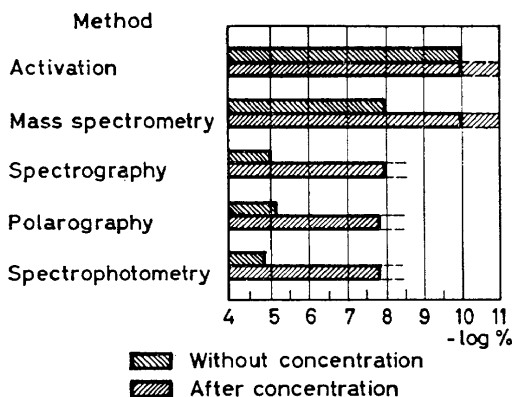


Figure 10. Effect of trace concentration

chambers with manipulators. It is certainly possible to "cool" the irradiated sample, but then a part of the radioisotopes will decay, and the sensitivity will be lower. In any case, a large number of data show that if the enrichment factor is satisfactorily high the base-element effect can be eliminated. The sensitivity of the determinations is then much higher (*Figure 10*), and their accuracy is improved.

CONTAMINATION AND LOSSES OF ELEMENTS IN THE PROCESS OF ANALYSIS

When working with highly pure substances a chemist is under very difficult conditions, as there are always many sources of contamination. Even in space the interplanetary gas contains about 1000 atoms in 1 cm^3; on the Earth's surface and in the air there are up to 10^{12} molecules and atoms in the same volume. In one cubic metre of the air milliards of atoms of the most common elements have been found. As a rule, the air of ordinary chemical laboratories contains Fe, Cu, Zn, Pb, Ca, Mg, Al, Si *etc.*

The experimentalist himself is often a source of contamination, as he may have gold teeth, rings, *etc.*; perfumery creams contain zinc oxide. A chemist must work with ultra-pure substances under so called "sterile" conditions. if we use the language of biologists, *i.e.* in rooms or boxes with a micro-climate and sterile air[18, 66]. It has been shown, for example, that by keeping the floor and the walls of the room moist, and the air pressure higher than the atmospheric pressure, it is possible to remove small amounts of calcium and other elements[1, 18].

Spectrographists know well that a curve showing the relation between intensity and concentration (*Figure 11*, curve 1) is often bent in the region of low concentrations (curve 2). This bend shows that the sample is contaminated with an element impurity from the air or from the electrodes (it is assumed that the background and overlapping with other element lines have been eliminated[18]).
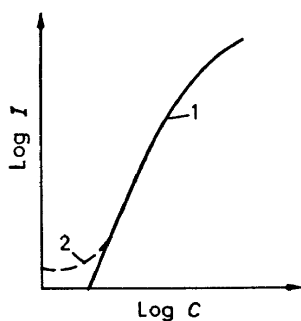
*Figure 11.* Effect of the sample contamination in spectrographic analysis

One of the sources of contamination is distilled water. It has been shown that distillation in quartz apparatus and electrodialysis are not enough for satisfactory purification[1]. The most effective is purification by means of ion-exchange with mixed ionites (Yoe and Koch) which can be easily seen

from *Figure 12.* Such water has the specific resistance of 15–25 Mohm/cm and contains not more than 10^{-7}–10^{-9} per cent of metal impurities[67]. It stands to reason, that this pure water may be stored only during a short period of time in a polyethylene vessel.
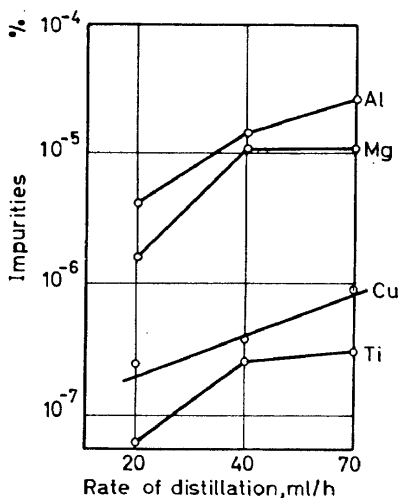
Figure 12. Purification of H_2O

Another, and I should say the most important source of contamination, is the reagents used. The most pure are organic solvents, such as benzene, carbon tetrachloride *etc.* The difficulties associated with the purification and storage of acids, alkalis and salts are much worse. Several papers have been published on this problem[68, 69]. I should like only to note that purity of acids depends on the rate of distillation, and also on the fraction which is used for the analysis (*Figure 13* and *14*). In a number of cases the reagents can be purified by the same method which is used for concentration and
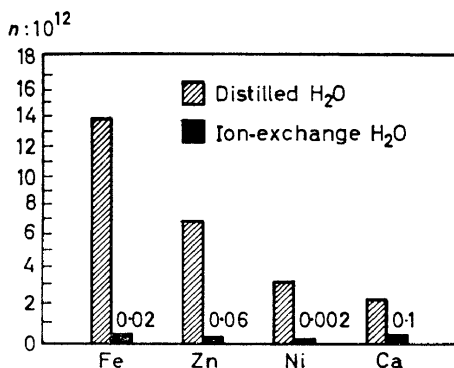
Figure 13. Relation between the impurities concentration in HF and the rate of distillation

determination of traces. If, for example, the element is determined by the extraction-photometric method, the reagents and water are purified before-hand by extraction with the same organic reagent, for example, with dithizone. Chemical ware and the time of storage of solutions should be
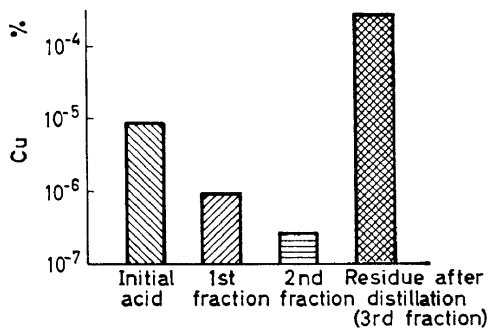

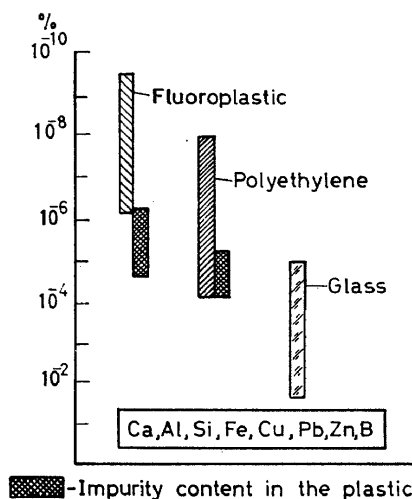*Figure 14.* Diagram of copper distribution in HF fractions

Figure 15. Impurity content in 0·01N NaOH after 30 days

considered as influencing contamination. We should remember that even the most pure quartz, polyethylene, or fluoroplastics contain noticeable quantities of metals[70,71] which are extracted differently depending on the vessel material and the nature of the element (*Figures 15* and *16*). In certain cases it is useful to coat the walls of quartz and glass vessels with hydro-phobic organosilicon compounds[72].

The average sample of the ultra-pure substance should be prepared very carefully. Sometimes, the sample should be washed before the analysis with highly pure acid or alkali to remove the surface impurities[73, 74]. Contamina-tion of the sample may occur during its grinding and this is very serious, as
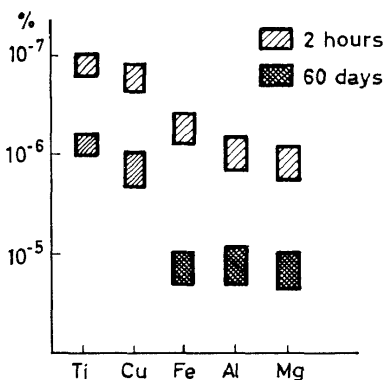
Figure 16. Spectrographic analysis of HNO_3 stored in a quartz container

it is difficult to correct by a control experiment, or "blank". In order to grind a sample of brittle material it is wrapped in a thin cellophane sheet and crushed with a press, or ground in a mortar made of highly pure quartz; agate mortars should not be used. The best procedure is to grind the sample between the plates of the same material. For example, it is suggested that semi-conductive silicon should be ground between the plates of pure quartz[75]. The advantages of this method are well shown in *Figure 17.*
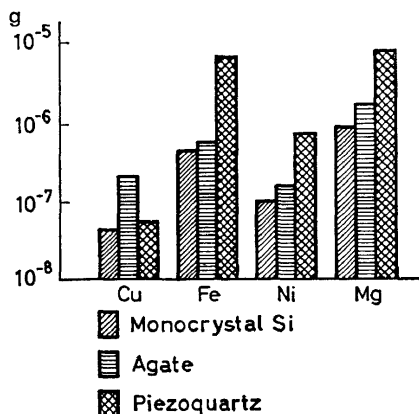

Figure 17. Contamination of semi-conducting Si during grinding

Besides contamination hazards, there is always a danger of losing the whole or a part of the desired micro-constituent during its concentration. Losses may take place when the element to be determined is in an unsuitable ionic state (complex compounds, polynuclear ions, molecules, colloids). Elements may be lost also by co-precipitation, co-extraction, volatilization as aerosols, *etc.* Stability of solutions and, particularly, absorption of traces on the container walls are also serious factors[76-78]. It should be mentioned that these problems have not yet been given sufficient attention.

Losses of trace elements are controlled mainly by means of radioisotopes, and the analysis results are corrected accordingly.

ACCURACY OF TRACE DETERMINATION

Problems of accuracy and reproducibility of trace determination by various methods have often been discussed in the literature. Nevertheless, it is not always possible to evaluate objectively various methods by these separated data. Unfortunately, up to now we have had very few experimental data on the comparative evaluation of the accuracy of methods applied in accordance with a certain programme to certain standard samples of highly pure substances. The accuracy of the results depends not only on the instrument and the method applied, but also on the correct preparation of the average sample, and its weight. Small samples which are used, for example, in mass spectrometric, spectrographic, or activation analysis lead to statistical fluctuations of the results due to the irregular distribution of admixtures in the sample.

As a rule, 1–10 g samples with preliminary concentration ensure greater reliability and accuracy in the determination of the average composition, on condition that the enrichment process is controlled with labelled atoms and all the necessary measures are taken to prevent contamination of the sample.

But, in spite of this, the decrease of trace concentrations involves the increase of errors, certainly, to a different extent for each method and element (see *Figure 18*). In various papers the accuracy of a method for trace
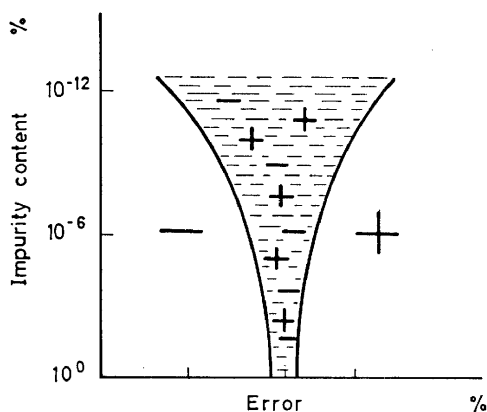
Figure 18. Fluctuations of errors as a function of impurity content

determination is estimated differently. For example, the results of the determination of 10^{-6}–10^{-7} per cent of impurities in pure silicon by the spectrographic method[79] give the mean arithmetical error within 25–40 per cent; when the determination is carried out by the neutron-activation method[1] the error is 5–10 per cent. Errors of the same order are observed
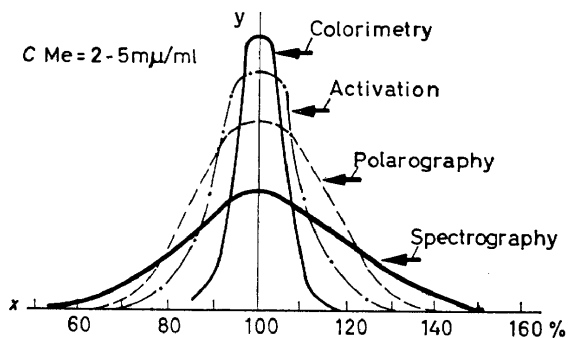
Figure 19. Accuracy of analytical methods

in the spectrophotometric analysis[80] (see *Figure 19*). Similar results on the accuracy of analytical methods are also given by other authors.

I should like to point out that, to a considerable degree, the accuracy depends also on the nature of the substance in which impurities are determined, on the proper preparation of standards, and on the precision of the instrument. Not the least of the factors is also the long-term experience of the analytical chemist which cannot be calculated by means of mathematical statistical formulae.

CONCLUSION

In this paper I have only been able to outline some aspects of the large and difficult problem of trace analysis. No doubt, some of the concepts suggests are open to discussion. Now we have reached a limit of about 10^{-9}–10^{-10} per cent, but it does not mean that this limit cannot be moved farther. One thing is obvious, progress in analytical chemistry, as in any other field of natural science, depends primarily on the readiness with which analytical chemists will use ideas and techniques from other branches of science.

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