# TRACE ANALYSIS APPLICABLE TO THE DETERMINATION OF MINOR IMPURITIES IN CHEMICALS. II - Analysis of high-purity mineral acids.

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## INTRODUCTION.

An extensive investigation directed among workers on trace analysis has shown the importance of analytical control of the chemicals used in industry and the laboratory. Important examples of industrial chemicals of high purity are nuclear chemicals, semiconductors, catalysts and metals. In the laboratory, it is principally analytical reagents that demand the highest purity ; one can cite "demineralized" water, the mineral acids and alkaline bases commonly used to solubilize samples, the solvents, and finally all the reagents involved in chemical separations or the formation of specific compounds.

Purity control may be envisaged under two aspects :

1. Detection of one or more defined elements, the presence of which is prejudicial to the use of the reagent in question ;
2. Systematic control of all the impurities.

In fact, the user of a particular product generally checks analytically for both these aspects, although very often he may be interested only in a defined number of elements. The case is different for the producer of the reagents, who must exercise control over the largest possible number of elements.

These two aspects stood out clearly in the above mentioned preliminary inquiry. Thus, for example, a particular laboratory may determine traces of boron in hydrofluoric, hydrochloric and sulphuric acids ; another laboratory may need to know the amounts of Cd, Pb, and Cu in phosphoric acid and acetic acid ; but often, the list of the elements is not limited. The methods have therefore to be chosen on the basis of the problem posed. Certain methods are preferred when the number of the elements investigated is limited (colorimetry, polarography, atomic absorption spectrometry) ; others are applicable to all the trace elements (emission spectroscopy, mass spectrometry). The methods used depend also on the amounts determined ; in other words, the choice of a method depends on its power of detection. The possibility of improving the limits of detection through a chemical separation of the elements to be determined, should also be mentioned.

Some of the results of this preliminary investigation are reported in Table 1.

The principal techniques employed and their scope of application to mineral acids, are discussed below.

## SEPARATION OF THE IMPURITIES AND METHODS OF CONCENTRATION.

The simplest method consists of separating the acid which constitutes the matrix by volatilization. This is easy, particularly for hydrochloric, hydrofluoric, nitric and acetic acids (Table 2), but not easy for phosphoric and sulphuric acids.

TABLE 1 : Classical methods in trace analysis.

| Acids analysed | Elements determined | Limit of detection µg ml$^{-1}$ (a) | Methods | Pretreatment |
|---|---|---|---|---|
| HCl, $HNO_3$, $H_2O$ | Rare earths, all traces | 0.01-0.1 according to the element | Spark spectroscopy | - |
| HF, HCl, $HNO_3$ | All traces | | Arc spectroscopy<br>Flame -do-<br>Mass -do- | Direct or pre-concentration. |
| Various mineral acids | All traces | 0.01 | Colorimetry, Emission spectroscopy, X-ray fluorescence | Direct or pre-concentration. |
| Mineral acids | Cu,Bi,Cd, Zn,Pb,Ti | 0.006-0.02 | Inverse polarography, Oscillo-polarography | Direct. |
| $HNO_3$, HCl | Au, As | 0.0001 | Activation | Extraction |
| | Ga, Cu | 0,001 | -do- | -do- |
| | Mo | 0,01 | -do- | -do- |
| | In,Zn,Sn | 0,1 | -do- | -do- |
| HF, $H_2SO_4$, HCl | B | 0,0002 | Fluorimetry | Distillation of the matrix |
| $H_3PO_4$ | Cd | 0,1 | Inverse polarography | Direct. |
| | Pb, Ca | 0,2 | -do- | -do- |
| $CH_3COOH$ | Zn, Cd | 0,005 | -do- | Distillation of the matrix |
| | Pb | 0,01 | -do- | -do- |
| | Cu | 0,05 | -do- | -do- |
| | Co,Fe,Ni | 1-5 | Atomic absorption spectrometry | |
| | Br | 1 | X-ray fluorescence | |
| Mineral acids | Ag,Ba,Ca,Cd<br>K,Mg,Cr,Cu<br>Mo,Ni,Pb,Sn<br>Te,Ti,Zn | 0,01 | Isotope dilution and mass spectrometry | Distillation of the matrix |
| $CH_3COOH$ | Na,Al,Fe | 0,01 | Activation | Ion exchange |
| | Cu | 0,001 | -do- | -do- |
| | Au | 0,00001 | -do- | -do- |

(a) µg ml$^{-1}$ = ppm ; ng ml$^{-1}$ = ppb.

Some losses for the elements As(III), B, Cr(III), Ge, Hg, Re, Ru, Sb(III), Se(II and IV) are inevitable, particularly if there is complete evaporation.

TABLE 2 : Distillation temperatures of some acidic solutions (°C).

| | |
|---|---|
| Hydrofluoric acid | 120 |
| Hydrochloric acid | 108 |
| Hydroiodic acid | 127 |
| Nitric acid (70 %) | 122 |
| Sulphuric acid | 330 |
| Phosphoric acid : decomposition at<br>($H_3PO_4 \rightarrow HPO_3 \rightarrow H_4P_2O_7$) | 213 |
| Perchloric acid | 200 |

No losses would be expected, however, for the following elements : Ag, Al, Ba, Be, Ca, Cd, Co, Cu, Cs, Fe, Ga, Hf, In, K, Li, Mg, Mn, Na, Ni, Pb, rare earths, Si, Ta, Ti, U, W, Zn and Zr. Distillation of the matrix is employed notably in emission spectroscopy (arc or spark); the sample can often be vaporized directly on the electrode. An aliquot of 0.25 - 0.5 ml (5-10 drops) permits limits of detection of 0.1 - 0.5 µg $ml^{-1}$ to be achieved for a number of elements.

For the application of methods of determination in solution it is also possible to evaporate a convenient volume of the acid to be analysed and then take up the residue in a minimal volume of water or in a suitable medium (acid or base).

Often a chemical separation of the impurities is necessary. Two methods can be used : precipitation and liquid-liquid extraction. The first method consists of precipitating the impurities to be determined, in the presence of a carrier. A combination of several reagents ensures the total separation of a large number of elements. For example, the sample (50 g) can be neutralized with ammonia and buffered with ammonium acetate ; the impurities are successively precipitated with 8-quinolinol, tannic acid and thionalide, and the precipitate is then ashed. Thus, the elements Ag, Be, Bi, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hg, Mn, Mo, Ni, Pb, Sb, Sn, rare earths, Ti, Tl, U, V, W, Zn and Zr may be recovered in a matrix of aluminium or indium oxide. This method, which was first suggested by MITCHELL and SCOTT (17), is much used in general purity control and has been described by a number of authors : HEGGEN and STROCK (7), PINTA (20), SILVEY and BRENNAN (24) and FALQUHAR et al. (5). Very often the determinations are carried out by emission spectroscopy (arc or spark), which permits limits of detection of a few ppb to be achieved.

The second method is based on the extraction of complexes by an organic solvent. The complexing agents most often used are dithizone, dithiocarbamate, rubeanic acid and cupferron, singly or in combination, when a group of elements has to be separated. Of course, for some elements, there are also much more selective reagents, e.g., nitroso-R salt for cobalt, diphenylcarbazide for chromium, 1,10-phenanthroline for iron, and dithiol for molybdenum. One method of total separation of the impurities in reagents depends on successive extractions with chloroform and methyl isobutyl ketone of the complexes formed with sodium diethyldithiocarbamate, 8-quinolinol and dithizone at different pH values. Thus, the elements Ag, Al, As, Au, Bi, Cd, Co, Cr, Cu, Fe, Ga, Hg, La, Mn, Mo, Ni, Pb, Pt, rare earths, Sb, Se, Sn, Ti, Tl, U, V, Zn, and Zr may be separated at levels of a few ppb (POHL, 23). MALISSA and SCHOEFFMANN (14) utilised ammonium pyrrolidinedithiocarbamate (APDC) as the extractant ;

this compound is capable of chelating some thirty metals which can then be extracted into organic solvents over a wide pH range. The method applied to the analysis of water by atomic absorption is described by ECREMENT and BARROIN (4) ; it is possible to concentrate the impurities by about 20-fold in volume and the extract prepared can be used directly for analysis by atomic absorption. The methods based on extraction of organic complexes have been described and discussed by KOCH (11), PINTA (20), MORRISON (19) and MINCZEWSKI (16).

Finally, the method of separating traces by distillation, which are applicable to volatile elements or elements that form volatile compounds like oxides, hybrides or halides, viz. As, Sb, Bi, Sn, Au, Mo, Ga, Cu, In, Tl, Pb, Se, Te, Zn, should be mentioned (MARCZENKO, 15).

The methods of concentration or separation of the impurities are not free from difficulties. The chief source of error is the risk of contamination arising from the complexity of the analytical procedures, and from the use of reagents often in large quantities ; this contamination is sometimes difficult to control. It is not always easy to run a blank, when analysis of an acid is attempted, unless it is possible to replace the sample by the same acid but of sufficient and known quality.

## METHODS OF DETERMINATION : COLORIMETRY, ABSORPTION SPECTROMETRY, FLUORIMETRY.

Determination by absorption spectrometry and colorimetry are in fact "individual" methods. Much used, they have tended to be displaced over the past dozen years, particularly by atomic absorption spectrometry. Nevertheless, from the inquiry conducted (22), it appears that these methods are still extensively used for a number of elements ; thus, in 1970 they were preferred for the elements As, B, Be, Cr, Fe, Mo, Ni, P, Sn and W. Table 3 indicates the methods for these elements and the limits of detection in solution.

Colorimetric and fluorimetric methods are easily applied to the analysis of acids when the number of elements present is limited ; it may be added that the extraction of complexes may allow an improvement in the limit of detection.
Some fluorimetric methods, listed in Table 4, also appear to be still used.

TABLE 3 : Analysis by molecular absorption spectrophotometry.

| Elements | Reagents | Limit of detection µg ml$^{-1}$ |
|---|---|---|
| As | Molybdenum blue | 0.02 |
| B | Quinalizarin | 0.05 |
| Cr | Diphenylcarbazide | 0.02 |
| Fe | 1,10-Phenanthroline | 0.05 |
| Mo | Thiocyanate | 0.005 |
| Ni | Dimethylgloxime | 0.1 |
| P | Molybdenum blue | 0.01 |
| Sn | Dithiol | 0.1 |
| W | Thiocyanate | 0.05 |

TABLE 4 : Fluorimetry.

| Elements | Reagents | Limit of detection $\mu g\ ml^{-1}$ |
|---|---|---|
| Al | Morin | 0.0005 |
| B | Benzoin | 0.04 |
| Be | Morin | 0.004 |
| U | Fused sodium fluoride | 0.0001 |
| Ga | 8-Quinolinol | 0.03 |
| Se | Diaminobenzidine | 0.002 |

## ATOMIC ABSORPTION AND FLAME EMISSION SPECTROMETRY.

These methods are convenient for the analysis of acids ; they are useful despite the necessary neutralization, and thus dilution, of the sample to be analysed. However, the acid matrix may also be evaporated and the residue taken up in water. LUNDY and WATJE (13) reported poor repeatability for the analysis of nitric acid and suggest evaporating 100 ml of the acid in the presence of 2 ml of sulphuric acid ; the residue (2 ml) is redissolved in water. Al, Fe, Cr, Ni and Zn are recovered completely, and 0.01 $\mu g\ ml^{-1}$ can easily be determined. Hydrochloric and hydrofluoric acids can be treated in the same fashion. Although it is more difficult, the procedure may also be applied to phosphoric and perchloric acids. The quality of the sulphuric acid serving as the support is important, but is easily checked by running a blank. The evaporation of the acid permits a 2-5 fold concentration of the impurities in the sample solution, so that limits of detection of 0.01 $\mu g\ ml^{-1}$ can be achieved for a large number of elements : Cd, Ca, Co, Cu, Fe, Li, Mg, Mn, Ni, Na, Sr, and Zn ; the limit of detection is 0.1 $\mu g\ ml^{-1}$ for Al, Cr, Mo, Pb, and K.

According to the elements required, flame emission or absorption spectrometry is used with air-acetylene or nitrous oxide-acetylene flames. The recently developed technique of flameless atomic absorption spectrometry is particularly efficient for the determination of elements at very low concentrations. The sample solution (10-100 µl) is evaporated at a convenient temperature (100-200°C) in the atomizer, and then the temperature is raised to 2000-2500°C, the atomic absorption being measured. Hydrochloric, hydrofluoric and nitric acids are easily vaporized without effect on the subsequent atomization. Sulphuric and phosphoric acids give off fumes during the evaporation-decomposition step providing non-specific absorption which is difficult to correct even with correction facilities for the spectral background. These difficulties are, however, not impossibilities. It is often preferable to evaporate diluted acid solutions (e.g. 10 %) rather than concentrated acids. It is convenient, for example, to start with 100 µl of 10 or 20 % (v/v) acid solution ; under these conditions, values from a few dozens to several hundred ng $ml^{-1}$ may be determined (Table 5).

TABLE 5 : Detection limits (in ng $ml^{-1}$) for some elements in acids (a).
(Flameless atomic absorption).

| | | | | | |
|---|---|---|---|---|---|
| Ag | 20 | Co | 400 | Na | 8 |
| Al | 200 | Cr | 100 | Ni | 400 |
| Ba | 400 | Cu | 40 | Pb | 200 |
| Bi | 300 | Fe | 200 | Pt | 2000 |
| Cd | 20 | Mn | 40 | Sn | 800 |
| | | | | V | 2000 |

(a) Samples of 100 µl of diluted (1 + 9) acid analysed with a Perkin-Elmer HGA 72 instrument.

Many other elements might equally well be determined with a high level of sensitivity, but data are still lacking.

The simplicity of the procedures with flameless atomization considerably reduces contamination risks. Very little work has so far been done on the analysis of acids for trace metals, but the numerous publications on the analysis of water may be consulted. It has been reported that the reproducibility of trace analysis in water can be considerably improved by the flameless atomization method, if the traces are separated by extraction of the complexes with ammonium pyrrolidinedithiocarbamate into methylisobutyl ketone and the extract is atomized directly (ECREMENT and BARROIN (4) and BOUCETTA (2) ).

## POLAROGRAPHY.

In general, classical polarography directly applied to the acid sample, simply diluted, is not sufficiently sensitive for the determination of trace elements. The elements to be determined must either be concentrated by evaporation of the acid, or concentrated as organic complexes ; the complexes must then be destroyed in an acid medium and the residue taken up in a convenient electrolyte (KCl, $NH_4OH$). Thus Cd, Co, Cu, Mn, Pb, and Zn can be determined (CARRITT, 3).

YASUMORI (25) utilised square-wave polarography for the determination of traces of copper, lead and chlorine in sulphuric acid.

However, the most sensitive method is inverse polarography (anodic stripping polarography). Electrolysis of the sample solution permits the deposition of the element to be determined in very small quantities ($10^{-8}$ - $10^{-9}$ M) on a hanging mercury drop cathode (KEMULA and KUBLIK, 8) ; the deposited element is then determined polarographically after the polarity of the electrode has been reversed, the variation of the anodic current with change in potential being recorded. The limit of detection of the method can be improved by increasing the time of the initial electrolysis. KEMULA and GLODOWSKI (9) have studied the determination of lead and copper (0.001 µg $ml^{-1}$) in concentrated nitric acid and hydrochloric acid by using a hanging mercury drop electrode ; the base electrolyte is 0.1 M nitric acid containing $5.10^{-7}$ gelatine. One of the laboratories which responded to the questionnaire in the preliminary inquiry, carries out the determinations under analogous conditions (anodic stripping and oscillographic polarography) in strong acids with the following limits of detection : Cu 0.006 µg $ml^{-1}$, Bi 0.02 µg $ml^{-1}$, Cd 0.001 µg $ml^{-1}$, Zn 0.006 µg $ml^{-1}$, Pb 0.02 µg $ml^{-1}$, Tl 0.02 µg $ml^{-1}$. The use of inverse polarography may perhaps be envisaged for the following elements :

Ba, Bi, Cd, Cu, In, Mn, Pb, Sb, Tl, and Zn ; of course, each element demands particular conditions of analysis.

## EMISSION SPECTROSCOPY.

In contrast to the preceding methods, which are very much restricted in the number of the elements that can be determined simultaneously, ultraviolet emission or spark-source mass spectrometric methods offer a much wider field of application, because of the possibility of detection and determination of some 30-40 elements in the same sample.

Emission spectroscopy with arc or spark as the source of excitation is actually the most accessible method and is consequently the most employed in the analysis of chemicals of high purity. Indisputably, the most sensitive method is arc spectroscopy:the solid sample is placed in the anode and excited under 10-30 A (d.c.). There are many practical techniques bearing on the operational conditions (PINTA, 20). For the analysis of acids, it is convenient to concentrate the impurities on a mineral support which serves as a spectral buffer. One very satisfactory method consists of evaporating a convenient sample (50-200 ml of diluted acid) in the presence of potassium or lithium sulphate (50 mg) ; the residue is mixed with graphite powder and spectrographed. If the sample is 25 g of the pure acid, the concentration factor is 500. In this way the following elements may be determined at a limit of 0.005 $\mu g\ ml^{-1}$ (5 $ng\ ml^{-1}$) : Ag, Al, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Pb, Si, Sn, Sr, Tl, V, Zn and Zr. KERSHNER et al. (10) have proposed an analytical technique for mineral acids by emission spectrography ; a sample of 100 g is mixed with 2 drops of concentrated sulphuric acid, 0.5 ml of 5 % (w/v) mannitol solution and 10 mg of graphite powder, and evaporated under an infra-red lamp in an atmosphere of nitrogen. The residue is spectrographed in an electric arc of 15 A in a controlled atmosphere. The limit of detection is 1 $ng\ ml^{-1}$ for several elements. These authors, who discuss the percentage recovery of some twenty elements, applied the method to hydrochloric, hydrofluoric, nitric and sulphuric acids.

Another strong excitation method, also much used, is the electric spark between graphite electrodes. The sample (10-20 g)is evaporated to dryness (see the conditions mentioned earlier) and taken up in the minimal volume of water (0.5-1 ml). One drop of this solution is placed on the plane section of each electrode (the total being 0.1 ml) and evaporated. The method has been described by MORRIS and PINK (18) ; with a capacitance of 0.005 µF and an inductance of 625 µH the following amounts in $\mu g\ ml^{-1}$ in acids can be detected : Al 0.0025, Sb 0.01, As 0.15, Bi 0.005, B 0.0025, Cd 0.02, Cr 0.001, Co 0.005, Cu 0.0005, In 0.01, Fe 0.002, Mn 0.00025, Mg 0.01, Ni 0.001, P 0.01, Ag 0.0005, Ti 0.0025, V 0.001, W 0.01, Zn 0.01, and Zr 0.0025. These values can be improved by taking a sample of 50 g.

Spark-source spectrometry permits direct analysis of solutions with arrangements rotating (rotrodes) or porous (porodes) electrodes. These methods, which are very sensitive for certain elements (Ag, Ba, Be, B, Ca, Cu, Fe, Li, Mg, Mn, Sr, Ti, Y ...), are directly applicable to an aqueous solution of the acid analysed, or again on an organic extract of the elements separated in the form of complexes.

Spectrographic (arc or spark) methods can also be applied after separation of the trace elements (precipitation or extraction).

## MASS SPECTROMETRY.

An increasing number of laboratories use spark-source mass spectroscopy for the detection and determination of traces ; this has come to light in the inquiry conducted (22). This method permits simultaneous determinations of many elements and, on this basis it may be validly compared to emission spectroscopy. Because of its high sensitivity, the spark is the most used source of ion production for trace analysis. It necessitates radio frequency (1 MHz) discharge in vacuum between metallic or graphite electrodes at a potential of 20-80 kV. The mass spectrum is recorded on a photographic plate or measured line by line with a detector. Originally applied to solids, mass spectrometry is today used for liquids. But still, it is convenient to evaporate the sample on the electrodes. The sensivity is very high ; on solids, the following amounts may easily be detected.

Al, B, Be, Ca, K, Mg, Na, P, Si, S : 0.001 - 0.003 μg $ml^{-1}$

Co, Cr, Fe, Mn, Ti, V : 0.004 - 0.006 μg $ml^{-1}$

As, Cu, Ni, Sr : 0.006 - 0.009 μg $ml^{-1}$

Ag, Ba, Bi, Cd, Cs, La, Mo, Pb,
Pt, Rb, Sb, Se, Sn, Te, Tl, Zn, Zr : 0.01 - 0.05 μg $ml^{-1}$.

Although the method is being utilized by many of the laboratories among those who responded to the inquiry, publications on its application to the analysis of acids do not seem to have appeared.

However, the paper of AHEARN (1) on the detection of impurities in liquids can be consulted. The chief difficulty stems from the heterogeneity of the residue of evaporation on the electrode ; since the impact of the spark is exact, this may result in poor repeatability of the measurements. AHEARN proposes a technique capable of giving a homogeneous deposit ; one drop of the sample (of convenient size) is suspended from the lower end of a silicon electrode of high purity, and evaporated in an electric field, the object of which is to maintain the liquid immobile. Application of the method to pure water permits limits of determination of the order of $10^{-9}$ g-atoms certain elements (As, Be) being accessible up to $10^{-10}$ g-atoms. At these very low values, a great risk of contamination exists ; it is indispensable to check the quality of the electrodes.

The conditions of application to the analysis of mineral acids merit study.

## RADIOACTIVATION.

This method is also used in the analysis of high-purity acids. This is certainly the most sensitive method available at the present time. When the sample is irradiated for an hour in a flux of 1.8 x $10^{12}$ neutrons $cm^{-2}$ $s^{-1}$ determinations of absolute quantities reach 1 ng can often be achieved by γ-spectrometry (GUINN and LUKENS, 6) : Ag, In, Mn, Re - 0.0001 μg ; Au, Cu, Ga, La, V - 0.001 μg ; Al, As, Br, Hg, I, Na, Sb, Sr, U, W - 0.001 μg ; Ba, Cl, Co, Ge, K, Ni, Th, Zn - 0.1 μg ; Ca, Cd, Fe, Mg, P, Pb, S, Sn - 0.1 μg.

These values can be improved by increasing the intensity of the neutron flux and the time of irradiation. Thus, values 100-1000 times lower still may be found in literature (KOCH, 12).

The above values are the absolute quantities detected in the aliquot analysed ; if the sample is 10 g, the detectable concentrations are the values divided by ten. This clearly shows that radioactivation is essentially the leader of physical methods of analysis as far as sensitivity is concerned.

A convenient chemical separation permits measurement of the activity of a "radiochemically pure" chemical. This separation is made after activation, by adding to the solution a known quantity of the element analysed in the same chemical form but inactive ; it serves as a carrier of the radioactive isotope to be measured. Thus, the risks of contamination are limited solely to the irradiation stage, and are therefore extremely slight ; from the irradiation stage only the radioactive fraction is important in the determination. It is understandable why radioactivation is perfectly suited to the analysis of mineral acids.

In one of the laboratories which responded to the inquiry, nitric and hydrochloric acids are analysed by neutron activation ; the elements are determined at the following concentrations : Au, As 0.0001 µg $ml^{-1}$ ; Ga, Cu 0.001 µg $ml^{-1}$ ; Mo 0.01 µg $ml^{-1}$ ; In, Zn, Sn 0.1 µg $ml^{-1}$. The elements are separated by distillation or extraction.

In another laboratory, acetic acid and distilled water are analysed for metals in the following ranges : Na 0.01 - 0.1 µg $ml^{-1}$; Cu 0.0001 - 0.1 µg $ml^{-1}$ ; Au 0.00001 - 0.1 µg $ml^{-1}$ ; Al 0.01 - 1 µg $ml^{-1}$ ; Zn 0.0001 - 0.1 µg $ml^{-1}$; Fe 0.01 - 1 µg $ml^{-1}$. Sodium and copper are separated by paper chromatography or by ion exchange. In spite of the attractiveness of the technique, its extensive application is limited by the sophisticated apparatus used : a neutron source is not available to many analytical laboratories, and still fewer have access to a reactor. This will limit the scope of application for a long time to come. However, one might also consider if it is really necessary to work routinely at such high sensitivities.

## CONCLUSIONS.

If the possible methods are compared, a selection can be rapidly made on considerations of cost of equipment and apparatus. Radioactivation is only possible for highly specialized laboratories. Is is almost the same for spark-source mass spectrometry, the apparatus for which costs around $ 100,000 and demands specialized personnel. Therefore, these methods will normally be used only when very high sensitivity, unattainable by other methods, is essential, or when it is necessary to check results obtained by other methods.

Emission spectroscopic techniques appear to be the most convenient for the determination of impurities in mineral acids of high purity, judged on the basis of the responses to the inquiry (22) as well as by the publications on the subject. Evaporation of the acid matrix makes it easy to achieve limits of detection of 0.01 - 0.1 µg $ml^{-1}$ according to the element ; indeed even lower limits are possible. Another advantage of these methods is that they permit simultaneous determinations of many elements.

Polarographic, colorimetric and atomic absorption spectrometric techniques appear to be employed mostly when the number of elements determined is limited and defined.

Finally, if the choice of the method is relatively easy, its application is not always without problems ; the notable causes of errors are *loss* by chemical treatments and *gain* by contamination. The use of very pure reagents is an obvious problem in analysing a product which itself is "very pure".

Difficulties often arise in the standardization of a method, particularly when a determination rather than a detection is required at levels of some ng $ml^{-1}$.

Physical methods offer a number of possibilities, but the scope of their application to individual cases is yet to be studied.

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# TRACE ANALYSIS APPLICABLE TO THE DETERMINATION OF MINOR IMPURITIES IN CHEMICALS: II—AN EVALUATION OF METHODOLOGY FOR THE ANALYSIS OF HIGH PURITY MINERAL ACIDS

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