

ISMA* Technical Conference

Helsinki, Finland
3-5 September 1963

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

DETERMINATION OF TRACE-ELEMENTS IN FERTILISERS

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The value of trace-elements in agriculture is regularly confirmed year after year, and international bodies of which ISMA is one, have far from lost interest in this problem which has already been the subject of several papers delivered at previous meetings (1-2).

By and large, however, the studies made have remained on the qualitative level and it is much rarer to find information giving precise figures in respect of soils before and after treatment and the fertilisers used when these various elements are missing.

The mutual interaction of concentrations of these metals at trace level have nonetheless frequently been stressed, so that it is now considered dangerous to add them without sufficient care.

It would appear that there is much work still to be done on the quantitative level in this field in order to specify agronomically the actual range acceptable in terms of the exact composition of the soil (macro and micro constituents) considered and, later, to enable an industrial study to be carried out on the homogeneity of various products treated with trace elements.

Analytical difficulties seem to lie behind the slow rate of progress in this field, in which one is frequently reduced to using semi-quantitative methods (arc spectrography in particular).

Moreover, the CENTRE INTERNATIONAL DES ENGRAIS CHIMIQUES (C.I.E.C.) only recently (3) drew our attention

to the lack of data on control procedures, stating that the studies undertaken in Ireland (where trace-element deficiencies assume tremendous proportions) had had to be "abandoned, at least for the time being, owing to this lack of references".

The problem of standardising the analysis of trace and secondary elements (S - Mg - Ca) has thus been entered on the agenda of this Body's next Congress (Zurich - May 1964). It would be abnormal if manufacturers of superphosphate, which may quite rightly be considered as a particularly well balanced fertiliser in this field, should be disinterested in this problem.

Analytical progress over the last few years has been sufficient to ensure that experimenters are no longer short of control equipment.

Without wishing to examine all the methods possible, let us briefly run over the techniques which we feel to be of special interest from the point of view of their rapidity, simplicity and accuracy.

Although direct physical examination (of the fertiliser or soil) may afford speedy information on the nature of possible deficiencies (arc spectrography - sometimes radiochemical activation methods), accuracy is generally obtained only after the solids have been placed in solution.

One has only to summarise the principal modern techniques to realise the wide range of possibilities available to the analyst today in the field of trace elements.

Before making a detailed examination of some examples which actually occurred in our laboratories, let us look quickly at the principles and characteristics of the chief methods more usually employed by us.

In each case, these have been selected with the triple aim of precision, specificity and maximum sensitivity, while avoiding the long and difficult classical separations that are more or less incompatible with the content level envisaged and the growing number of checks called for in all fields.

Sufficient specificity can, however, be attained only by combining two or more techniques, themselves already selective, which then play the part of punched cards superimposable in a single chemical operation. The main cards at present available to the analyst allow for an almost infinite variety of combinations, although it is becoming increasingly rare to have to resort to prior separations, more or less in groups, as characterised the traditional methods of a few years ago.

1 - METHODS OF TRACE-ELEMENT ANALYSIS

1. - COMPLEXOMETRY AND THE GENERALISED USE OF COMPLEXES

with various, mainly organic, molecules.

There scarcely exists an inorganic ion which cannot under certain conditions be selectively complexed to a greater or lesser degree. There is a very wide choice of reagents which is increasing every day. Parallel to this, great progress is being made in studying the specificity of the bonds and determining dissociation constants. We may therefore hope that it will soon become possible to connect the almost infinite number of possible reactions by means of a few general rules that are clearer and more precise than the qualitative indications at present provided by the radius, charge and electro-negativity of the inorganic ion under study and the acidity of the organic reagent.

It should be stressed that the selectivity of each reagent can generally be improved by modifying the respective concentrations in solution through a careful choice of the pH factor (working on the dissociation constant of the complexing compound or complex, or on the solubility product of the hydroxide corresponding to the element present or of the Redox factor (change in the state of oxidation of certain ions ..)).

Although a large number of functional organic groups

characteristic of various ions have so far been specified it is still too early to classify reagents on the basis of this incomplete data. It is still only possible to group them in restricted homologous series within which they differ only in various substitutions. Some of them deserve special mention owing to the frequency with which they are used and their value in determining trace-elements.

A - Polyacid amine group - Complexons

These reagents are very often used to suppress troublesome interference by enabling the ions involved to be complexed. In general, they have been subjected to very searching study and, through our knowledge of all the dissociation constants, it is now a simple matter to define the ideal conditions of use in each case, particularly for limiting the concentration of a troublesome ion to a level below that at which interference begins. Numerous reagents of the same type have been in common use for several years.

Firstly, there is ethylenediaminetetraacetic (EDTA) (Complexon II), the best known and one of those which give the most stable complexes.

Diethylenetriamine pentaacetic acid (DTPA) is found capable of complexing Fe^{2+} , Fe^{3+} ; Co, Ni, Cu, Zn, Cd, Pb, Hg and Ca still better.

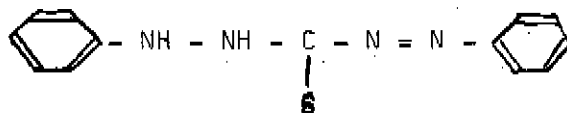
Interference by alkaline-earth metals may generally be reduced by using ethylene diaminedipropionidiacetic (EDDPDA) and ethylenediaminetetrapropionic (EDTP) acids in which enlargement of the chelation ring is less compatible with the formation of alkaline-earth complexes.

Other compounds of the same type deserve particular attention in certain special cases :

thus, ferric complexes of HEDTA (N-hydroxyethylethylenediamine triacetic acid) and HEDDA (NN'-dihydroxyethylethylenediamine diacetic acid) are not, contrary to the corresponding EDTA complex, hydrolyzed with precipitations of $Fe(OH)_3$ at alkaline pH values.

We shall not enlarge any further upon this list, which is growing longer every day and thus affords a great number of possibilities.

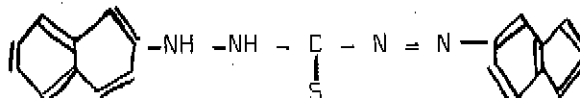
B - Dithizone group -



As dithizones have been known for over 50 years and are fairly universally used, there is no need to list their properties in great detail. Let us simply stress that their use may now be justified a priori by the logical use of dissociation calculations particularly in relation to the pH factor. Deep theoretical study has in fact been made, and there are now several books available giving all the useful constants. We should mention however that they are very difficult to use in spectro photometry owing to their high oxidisability.

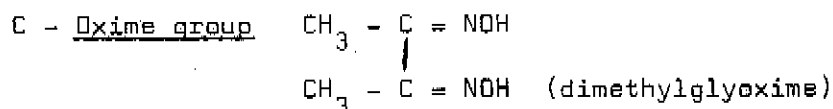
We frequently use dithizone as a means of separation; it is a particularly selective and convenient solvent as its subsequent decomposition takes place very quickly upon simple evaporation in the presence of H_2O_2 and H_2SO_4 .

Sensitiveness may be even further increased by using di- β -naphthylthiocarbazono



particularly for Zn, Cu and Hg.

Finally, thanks to its great stability as a reagent, O-ditolylthiocarbazono shows great prospects for development.



Dimethylglyoxime was one of the first organic reagents to be used in analysis.

The possibility of solvent extraction of the coloured complexes formed with various metals has fostered its

development in the field of trace-element analysis.

The nickel compound may be extracted by chloroform in an alkaline or slightly acid medium.

Then again, Pb may be separated in an acid medium. The use of this reagent is not restricted to these elements; indeed, it has given great service in the determination of Rhenium.

We should also stress that a water-soluble compound more sensitive than Ni^{2+} may be formed with Ni^{++++} .

The sensitiveness, and particularly the extractability of the Ni^{2+} may be improved by using oximes like furil dioxime or cyclohexane dionedioxime, although this reduces selectivity.

Selectivity may also be improved with ~~ox~~ benzoineoxime in the case of trace-elements Mo and W.

D - Oxine group

Like dithizone, oxine (8-hydroxyquinoline) is well known to analysts, although it seems to have been used much less in the field of trace-elements. This relative disaffection may be explained by the insolubility of the complexes formed in water, and by their generally rather dull coloration. However, it is possible to extract them more or less selectively by organic solvents on which it is becoming possible to carry out either spectro-photometry (not very specific as a rule, except in the case of iron and vanadium which are the only elements to give colorations other than yellow) or fluorimetry.

Sensitivity may be improved by using substituted derivatives:

- 5- iodo-8 hydroxyquinoline chiefly for Cu, Mn, Co, Ni and Fe -
- 5 (or 7) - methyl - 8 - hydroxyquinoline for Zn, Mn and Co
in the case of extraction by carbon tetrachloride or benzene,
dibromo hydroxyquinoline for copper.
- 5 - methyl - 7 - nitroso - 8 - hydroxyquinoline etc.

Generally, however, this improvement in the sensitivity often goes hand in hand with decreased selectivity. The opposite effect (improved specificity at the cost of a slight reduction in sensitivity) is obtained by substitution by a nitroso group as in 5-nitroso-8-hydroxyquinoline, or by steric hindrance in the case of 2-methyl-8-hydroxyquinoline which does not react with Al, Y, Ga, In or Tl.

E - Dithiocarbamate group - $R_2N - C \begin{matrix} \diagup S \\ \diagdown S \end{matrix} -$

Although less classical, these reagents are nonetheless particularly interesting due to their relatively higher specificity. Diethyldithiocarbamate has proved to be the favourite reagent in determining traces of copper in most cases. It can also be used at the same time to determine Ni and Bi. However, it cannot be used in the presence of high Fe, Bi, Ni, Co and Mn contents.

Better specificity is obtained by using homologous compounds capable of introducing a steric factor of the acetanilide dithiocarbamate, phthalimidedithiocarbamate, succinimide dithiocarbamate and pyrrolidinedithiocarbamate types.

Finally, it is possible to work on the pH extraction as with the preceding reagents. We should stress that we use diethyldithiocarbamate in specific conditions for copper by effecting the extraction with isoamyl alcohol in the presence of EDTA and in an ammoniacal medium.

Let us now leave this list, which could in itself provide the subject of several books. We have voluntarily restricted ourselves to a few examples which represent only a fractional part of the range of choice available at present in this field.

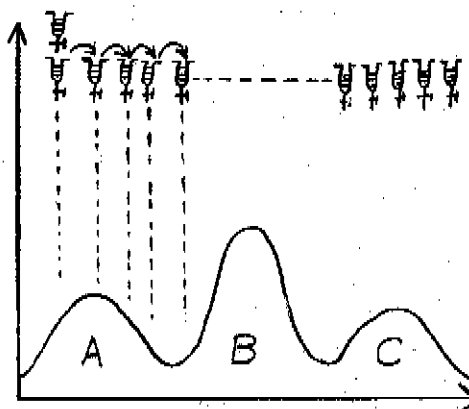
2) - EXTRACTION BY SOLVENTS

Complexes formed with the various reagents are more or less soluble in water or other solvents. The often very great difference in the solubility of various complex ions frequently enables one to plan their separation by extracting one of them with a suitable solvent in a simple

separating funnel. Suitable pH and Redox factors may also favour the results at this stage. In a fair proportion of border-line cases, however, simple extraction is not enough, although it is possible to separate the undissociated elements by a simple extraction, in effect, a fractional separation in accordance with the attached drawing, for example:

This method (the Craig method) is well adapted to automation and mechanised equipment is already on the market.

When the various tubes are examined at the end of the operation the various complexes are found to be distributed in the shape of a bell.

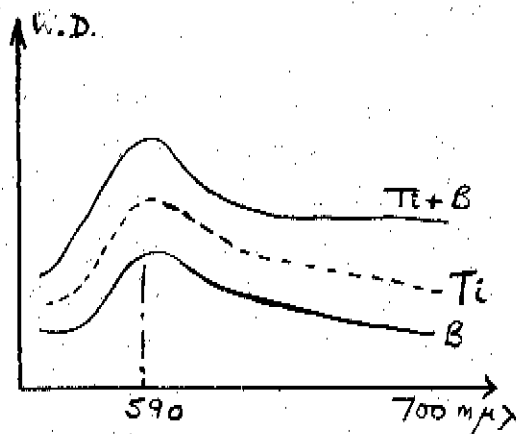


3) - SPECTRO-PHOTOMETRY

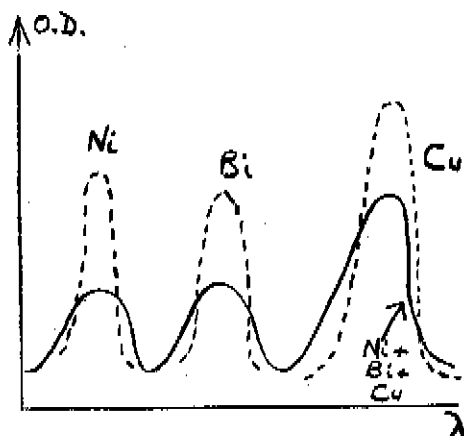
Based on the selective absorption of the chromogenic groups of some complexes, this technique is still one of the most important in the field of trace-element analysis.

As the maximum absorption frequencies are often characteristic of the complexed element, it is frequently possible to determine several ions simultaneously.

For example, diethyl-dithiocarbamate with Ni-Cu - Bi may give complexes that can be extracted under the same conditions.



By measuring the optical densities at the three wave-lengths λ_{Ni} , λ_{Bi} , λ_{Cu} , we can calculate the three concentrations by means of a system of 3 equations with 3 unknowns. However, this method holds good only when the respective concentrations are of the same order



Thus, it is possible to determine more easily, more accurately and more frequently traces of B in the presence of titanium by carminic acid.

Apart from the choice of wave-length, it is often possible to increase sensitivity by modifying the medium : addition of miscible solvents, alteration of the proportion of reagents or extraction by means of a suitable solvent. Similarly, the specificity may be modified by altering either the pH factor or the redox potential.

It would appear that one of the principal factors behind the progress made in recent methods has been the precise fixing of the pH factor (± 0.1 pH). In the old methods, undue confidence was often placed in the stabilisation of the pH factor by the addition of various buffer solutions.

4) - FLAME PHOTOMETRY

In its most general sense, there are two variants of flame photometry :

α) The emission method used chiefly in determining alkalis; and)

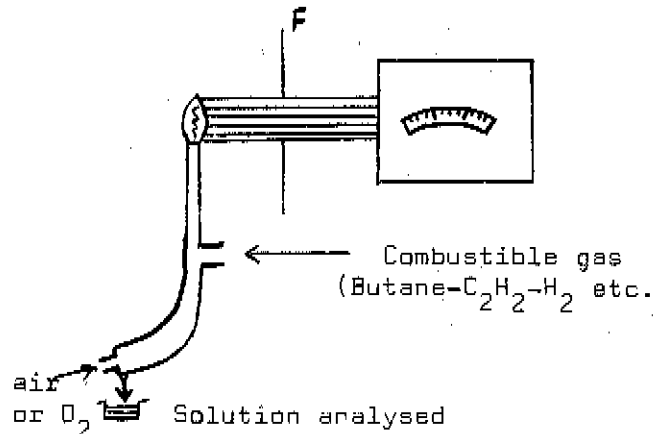
β) The absorption (atomic absorption) method, still largely undeveloped in the chemical industry.

This method is found to be very sensitive, rapid

and accurate. Moreover, the equipment required is relatively cheap. We have sought to develop this particularly promising technique to the full, for it seems destined for wide application. Although still in the development stage, it has already been of great service to us and we feel that it should be given special emphasis in this general report.

A - Emission

The apparatus depicted here consists of an atomizer for the solution to be analysed, a burner and a device for analysing the radiation emitted, a monochromator (or simple photo-electric cell fitted with a filter in certain simple cases (alkalis - alkaline earths)



At the temperature of the flame, a number of atoms present in the atomized solution are excited by the movement of an external electron from energy level *s* to levels *p* and *d*. This corresponds in fact to an abrupt deformation of the electronic orbit, which takes on a circular form with stronger potential energy.

In falling back to its original *s* level, the electron emits this energy in the form of radiation with the corresponding frequency. Because only the external electron levels are involved the energy liberated is relatively small, so that the corresponding frequency falls within the visible or near-visible spectrum.

This gives flame spectro photometry an advantage over arc or spark spectrography which, owing to the greater amounts of energy liberated, work mainly in the ultra-violet. The optical equipment may consist entirely of glass, this affording a reduction in cost.

Another more important advantage lies in the small number

of rays emitted (only the outermost level or levels being involved); this gives greater specificity and simpler application by doing away with the use of the very large resolving powers which chiefly account for the high cost of spectrographic equipment.

This is a tremendous simplification in the special case where the major element is one of the transition metals which give very elaborate arc spectra.

A third advantage lies in the fact that the flame is easier to stabilise, so that precision is greater (e.g., see the AFNDR Standard for the macrodetermination of K_2O in fertilisers, which affords relative precision of the order of 0.5%).

On the other hand, the product analysed must be placed in a solution beforehand. Then again, as the concentration of the solution is limited by the risk of blocking the atomizer, sensitiveness is often somewhat lower, particularly with "cold" flames (butane + air)

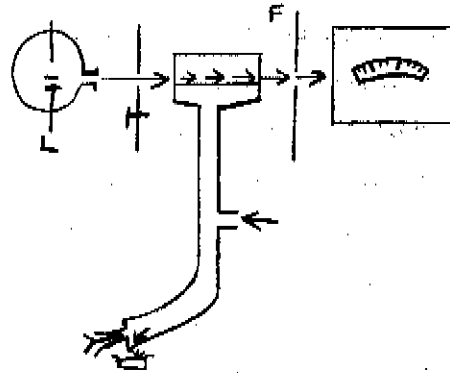
Sufficient sensitivity is only obtained by using a hotter flame (oxygen-acetylene or oxygen-hydrogen instead of butane and air), but it is then possible to determine concentrations of from 1 ppm to about 5% provided that essential precautions are taken to avoid interference.

This interference, although less serious than in spectrography, becomes of vital importance when the flames used are very hot, owing to parasite mutual enhancement caused by collisions with foreign atoms. It is then essential to refer to dial-readings obtained in the presence of similar concentrations of the major elements; as solutions are involved, this generally entails no practical difficulty.

B - Absorption

The apparatus is similar to that used in the emission process, but includes a monochromatic source corresponding to the emission of the element to be determined (hollow

cathode lamp). However, the burner is larger and an additional system of modulation may in certain cases be connected to the measuring equipment to enable the phenomena of absorption and emission to be separated, thus serving to improve sensitivity.



The unexcited atoms in the flame may become excited not only under the effect of the temperature of the flame, but even more readily when they are irradiated by a radiation at a frequency which corresponds to the principal ray emitted.

This process affords great sensitiveness in the case of atoms which it is difficult to excite by means of the flame.

This method does not give rise to the mutual interference which may exist in the emission method.

Such interference by the major compounds present is relatively important in the emission process as it affects the percentage of excited atoms measured.

With atomic absorption on the other hand, it is the strength of the unexcited atoms present in the flame which is measured; as the percentage not excited is generally very high, the above error will be negligible in terms of relative value.

This, coupled with the greater reproducibility of the absorption phenomenon (which is less sensitive to local temperature fluctuations within the flame), affords greater precision in most cases.

Without going into detail on the results obtained by Mr. THILLIEZ, Instrument Engineer in the Analytical Department of Ets. KUHLMANN's Central Laboratory, we would just mention that this method is of great service to us in determining magnesium, both as regards its sensitiveness (0.01 ppm in solution), and its accuracy (nearer than 1% relative with solutions of 2 ppm) and specificity.

The same prospects arise, except as regards sensitivity, for the trace-elements, zinc and copper, to mention only the main ones studied.

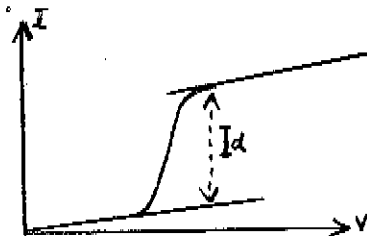
This method is, in fact, generally used and, in future, will no doubt enable most series checks to be advantageously worked out with great precision.

5) - ANALYTICAL ELECTRO-CHEMISTRY

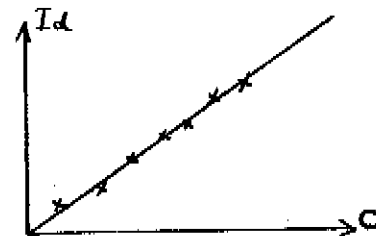
Irrespective of the essential selective role constantly played by the pH and Redox factors, analytical electro-chemistry allows for fairly general methods of determination, despite their high specificity.

In particular, these are as follows:

Classical polarographic methods are recommended, but we shall not dwell on the principle involved.



Let us simply mention that the electrolysis current produced by the discharge of the ion to be determined at a given potential, is measured at the point of equilibrium.



This current is limited by the diffusion of the ion towards the electrode, and is thus proportional to its concentration. With normal equipment, sensitivity is generally between 0.1 and 1 ppm.

The precision afforded is also very high (2 to 5% relative). As each ion has its own characteristic discharge potential, this method is highly specific and trace interference fairly infrequent.

We should stress that sensitivity may be even further improved in the case of ions capable of being deposited in the metallic state and amalgamated, by means of the hanging drop procedure. The impurities to be determined are concentrated on a fixed drop of Hg and then redissolved by inverting the polarity of the mercury. For

a given pre-electrolysis time, the current produced in this anodic redissolution is proportional to the concentration in the initial solution, which may thus be measured to 10^{-8} M without difficulty.

This technique, which has been studied in the Analytical Department by Mr. BOURROUILH, the Engineer responsible for electro-chemical methods, is particularly suitable for checking Pb, Bi, Cd, Zn and Cu.

6) - INTERCHANGE OF IONS

We shall deal briefly with these methods.

However, let us mention that, on the industrial plane, the practical use of radio-elements is somewhat limited by the special precautions required and the high cost of irradiation at the present stage of development of the sources.

Nonetheless, emphasis should be laid on the extreme sensitivity of these methods, which are still by far the most advanced in this field.

11 - DETERMINATION OF THE MAIN TRACE-ELEMENTS **

Co, V, Se and W, to mention only the elements most frequently referred to, have now been added to the list of six micro-elements (Fe-Mn-B-Zn-Cu-Mo) considered since 1955 as being essential.

In view of the analytical experience acquired by Ets. KUHLMANN's, Analytical Department in the field of trace-elements, particularly during its studies of pure metals, nuclear products and pigments, it has been a relatively simple matter to select suitable procedures for checking them accurately and rapidly, whether in fertilisers, soils or plants.

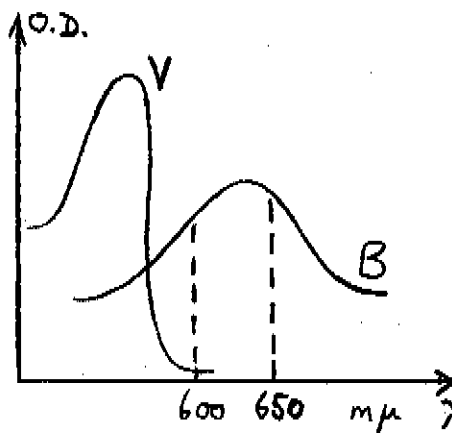
** We would emphasize that the sensitivities mentioned in this article for spectro-photometric methods are for cells 1 cm thick; in practice they may be improved by a factor of 5, by using a 5 cm cell.

In the following pages we shall endeavour, without trying to cover the subject too thoroughly, to restrict ourselves to setting out, element by element, the conclusions we have drawn and the chief methods we finally had to choose in practice.

DETERMINATION OF BORON -

Although micro-chemical determination is relatively simple and conventional (acidimetry after distillation), the micro-determination of Boron often presents a difficult problem, particularly when very high sensitivity is required.

Apart from spectrographic techniques which enable solids to be checked rapidly and with great sensitivity (a few tenths of a ppm) but often with a lack of precision, the analyst has numerous wet-test methods at his disposal (spectro photometry, flame photometry etc.,). Of these we have come to prefer spectro photometry of the complex obtained in a sulphuric medium with carminic acid[&], which gives reasonable sensitivity (0.1 to 1 ppm in solution depending upon the case involved), acceptable precision (10% on 10 ppm) and a wide range of application (4).



Nitrate and nitrite interference is eliminated by heating with HCl beforehand.

As mentioned earlier, the influence of the titanium was simply removed by taking a double spectro-photometric measurement. The same applies to vanadium if the measurement is effected at a suitable wave-length (see

&. Other spectro-photometric methods have not the simplicity of use of carminic acid: marked effect of H_2SO_4 concentration (quinalizarin) or delicate and not very specific application (curcumin) requiring difficult distillation beforehand.

above drawing). This method is therefore highly specific. In particular, no interference is caused by : U-Cr-Al-Zr-Ni-Fe-W-Nb-Ta-Si-Ge-Mo-Ce- PO_4^{---} , F-Ca-Cl-Mg-Na-K.

When applied to sulphuric acid, one attains a limit of the order of 0.1 ppm; on soils and fertilisers, 1 ppm is easily detected.

In the case of pure waters, we have been able, thanks to this method, to determine up to 0.01 ppm to nearer than ± 0.005 ppm by concentrating 50 ml beforehand in a platinum capsule.

In fertilisers themselves, which may through intentional addition contain high proportions (at least 1%), it may be determined by conventional methods of distillation; however, we prefer the simpler, quicker and less tricky method consisting of simple extraction by water saturated with carbon-dioxide at about 80° (not more, or Boron is lost), followed by conventional titration with mannitol after the phosphate ions have been separated by means of Bismuth nitrate and the NH_4 removed by boiling in an alkaline medium (5).

This method can be applied to fertilisers rich in fluorine (superphosphates) if one takes the precaution of starting the extraction process cold with a few millilitres of a concentrated acid solution of aluminium chloride which enables this element to be complexed, thus avoiding the formation of Boron trifluoride, which is particularly volatile.

DETERMINATION OF COBALT -

So far, this element has chiefly been determined in soils by means of arc spectrography following various more or less long and difficult processes of enrichment often based on organic precipitations that frequently required the addition of coprecipitating agents.

However, this element may be determined with precision in a solution, by using a reagent which is of particular interest in cobalt spectro-photometry. Nitroso R Salt has for a long time been held by our laboratories to be

the ideal reagent for determining this element, both in pigments and in various materials of a nuclear structure.

This opinion is today shared by numerous authors, including the team of Prof. MONNIER in Geneva, who wrote in 1961 that this method is "the most sensitive, the most precise and one of the fastest known" (6).

Spectro-photometry may be made completely selective if separation is effected beforehand, either by an interchange of ions or by extracting the dithizonate with CCl_4 . The use of dithizone as a separating process has been found by us to be entirely satisfactory, as the dithizonate is readily and completely decomposed by the simultaneous action of concentrated H_2SO_4 and H_2O_2 .

Now perfected, this method of operation enables strengths as low as 1 ppm in solution to be determined within an accuracy of about 10%, and within an accuracy of a few per cent in the case of strengths of the order of 50 ppm. If the fertiliser or soil studied is rich in precipitable elements with a pH factor of 7, at which the dithizonate is most easily extracted, the method may still be applied by effecting the extraction in a medium containing citrate at about pH 6.5.

This method is particularly well suited to the analysis of soils or rocks containing strengths of between 0 and 50 ppm, with an average of about 10 ppm, but it is also applicable to products which contribute trace-elements to agriculture, such as fertilisers and various silicates specially manufactured for the purpose.

A second method based on colorimetry of the extract (by isoamyl acetate) of 2-nitroso-1-naphtholate of cobalt may also be applied to products which do not contain too much ($< 1\%$) Copper, Manganese, Nickel or Tin, as is generally the case in agriculture (7). This process does away with the need for prior extraction by dithizone, but requires numerous washings of the organic layers extracted, either to improve the stability of the complex or to

reduce interference from the various heavy metals (particularly copper).

DETERMINATION OF IRON

We do not propose to go too deeply into the methods of determining this element as they are sufficiently well known and all the more numerous as the iron content of fertiliser and soil is always relatively high.

This often enables us to make an oxido-reduction titration (we recommend that the hydroxides be precipitated, dissolved in concentrated HCl and then titrated, after reducing with Cl_2Sn and the slight excess eliminated by adding mercuric chloride, with potassium bichromate solution using barium diphenylamine sulphonate as the indicator. This method is applicable and extremely accurate (1% relative) for strengths of more than 0.01%.

Below this figure, a wide range of colorimetric methods may be used; in making special reference to the α, α bipyridyl method, we would mention that this conventional system may be vitiated by numerous elements and that, under these conditions, when dilution is not very great, it may be better to use the more specific and sensitive Bathophenanthroline.

DETERMINATION OF ZINC -

This element gives only a few selective coloured complexes; only zincon and $\alpha\beta\gamma\delta$ - tetraphenyl-porphine are capable of being used in spectro-photometry, but prior separation is generally necessary owing to numerous interferences.

We have managed to perfect a method sensitive to 1 ppm in solution, giving a degree of precision of the order of a few % relative, with strengths of about 50 ppm, consisting of separation by ion exchange followed by spectro-photometry of the zincon complex.

The anion exchange resin (DOWEX 1) used fixes the zinc selectively in a hydrochloric medium of suitable concentration.

It has then only to be washed out by a very dilute hydrochloric acid to obtain a pure solution of zinc that is treated by the Zincon direct.

No trouble is given by the ions generally found in soils and fertilisers, such as Mn-Mg-Al-Ca-P₂O₅-Na₃-K-Na-NH₄-Ti-Fe-Cr-V^{IV}, etc.

Copper only begins to give trouble when its presence is between 5 and 10 times greater than that of the zinc. Vanadium is troublesome in the 5⁺ state, but may easily be reduced to V^{IV} beforehand by SO₃Na₂.

Finally, we also have three other fast and highly sensitive methods, all of which afford satisfactory precision.

Flame absorption has enabled us to reach, practically without interference, 0.01 ppm in solution, i.e. we have had no difficulty in attaining 1 ppm in soil or fertiliser, and an accuracy of 2 to 3% on 1 to 2 ppm in solution. A recent article also relates to similar performances (sensitivity of 0.03 ppm) (9). Hanging drop polarography is capable of affording even greater sensitivity if required (particularly for determination in plants). A second advantage is that copper may also be determined simultaneously.

Conventional polarography, although less sensitive (~~#~~ 1 ppm in solution), makes it possible to determine zinc, copper and manganese, in a medium of ClNH₄ + NH₄OH, simultaneously in one and the same operation (8). In reality, and contrary to the assertions of literature, the determination is effected not by the zinc but by the sum of the zinc plus the cobalt. One has only to make a second polarogramme in a sodium tartrate medium with a pH factor of 8 to obtain the zinc alone and, by comparison with the polarogram effected in the ClNH₄ + NH₄OH medium, find the respective concentrations of zinc - Co - Cu - Mn.

In conclusion, we would stress that important traces of zinc are found again in numerous reagents, particularly pure HCl, thus making it necessary to systematically prepare blank tests.

DETERMINATION OF COPPER

Extraction of the complex with diethyldithiocarbamate or dibenzoyldithiocarbamate (arazate) (12) can be made specific in the presence of EDTA; thus, the spectro-photometric treatment of these complexes in isoamyl alcohol is a favourite method, fast, accurate (5% at the 10 ppm level) and highly sensitive (1 ppm)

Similar performances are obtained by using oxalyl dihydrazide, despite the higher value of its coefficient of molecular extinction (10), as the complex is not extractable. This lack of extraction accelerates determination but may frequently limit the method's application (unfilterable cloudy solutions - presence of colloidal or highly coloured organic matter, etc.,). We also note that this method is impaired by over-strong concentrations of Co or Mn⁺⁺.

Finally, we would mention two other colorimetric reagents : cuproine (2-2' diquinoline) and neocuproine (2-9-dimethyl 1-10-phenanthroline); though both very specific, it appears that they are less sensitive (2 to 5 ppm) (11).

Numerous other colorimetric methods written about so far are of less interest than the three described above, either because they lack sensitivity (amines-ammonia-benzoin oxime-complexons - Tiron, etc.,) or because of their lack of specificity (biocylcohexanonoxalylidihydrazone: interference of Co -T.E.T.R.A. - o,o-diisopropylphosphorodithioate, etc.,).

Spectro-photometric methods used on solutions are not the only ones possible for this element, however.

We must emphasise the possibilities of flame photometry (by emission and, above all, by absorption), which gives a sensitivity limit of 0.1 ppm in solution, i.e., 1 ppm on the product, as well as those of conventional polarography or the hanging drop method.

In the two last-mentioned techniques, the same solution may be used for determining several other elements :

by flame absorption : Cu-Zn-Mg-Mn and Co with slightly lower sensitivity;

by conventional polarography (see Chapter on Cobalt above) : Cu -Co -Mn -Zn; and -

by hanging drop polarography : Cu -Zn.

DETERMINATION OF MANGANESE -

Traces of Manganese may be determined by polarography simultaneously with Co-Zn and Copper, as explained in the Chapter on the determination of Zinc. It is also very easy to make accurate and sensitive determinations by flame absorption.

Finally, it is possible to make specific colorimetric determinations by using oximes (formaloxime - carboxy 4-isonitro-isoacetanilide, etc.), which, with Mn^{++} in an alkaline medium, give red/brown complexes of the ion Mn^{3++} . Sensitivity to traces of Fe makes separation necessary; this may be effected simply by the use of an ion exchanger.

Formaloxime in an ammoniacal medium seems to be the most sensitive reagent available at present (0.02 ppm in solution). We normally use it, after separating the Mn on DOWEX 18 X - 50/100 mesh, if the Iron content is high; (in a 12 N HCl medium the Mn-hydrochloric complex is fixed; it is washed selectively with 6 N HCl Fe-Co and Cu remaining fixed on the resin; Mg and calcium are eliminated with the effluent of the 12 N HCl during the fixing process and cannot therefore precipitate subsequently in the ammoniacal medium).

The same method has been applied with benzohydroxamic acid, which seems to give a similar reaction (13).

A recent method also appears to be attractive; in this, the resin separation process is done away with thanks to the selectivity of the coloured reaction obtained by extracting the tetraphenylarsonium chloride + permanganate complex with chloroform. Potassium periodate is used to oxidize the Mn^{++} beforehand (14). It

should be stressed, however, that this method is less sensitive than the formaldoxime reaction (limit of 5 ppm if 1 cm spectro-photometer cells are used : 0.5 ppm in solution).

Finally, it is also possible to carry out colorimetric determination with benzidine after oxidisation by periodate, although the sensitivity is limited (0.25 ~~mg~~ /ml) and the instability of the measurements calls for very exact timing which is applied only with difficulty.

DETERMINATION OF MOLYBDENUM -

As in the case of most of the preceding elements, molybdenum may be determined by means of polarography and flame spectro-photometry.

The polarographic method (in a nitric or perchloric medium) requires that the molybdenum be separated beforehand by α benzoin oxime and chloroform and is not very sensitive with the conventional apparatus (10 ppm).

According to the literature, flame absorption affords a limit of 0.5 ppm in solution (i.e., a maximum of 5 ppm in fertiliser or soil). We have made no measurements by this technique so far, in this particular case.

Much greater sensitivity is in fact obtained by spectro-photometry of the complex formed with dithiol (4-methyl 1-2^d-dimercaptobenzene) (18) (0.04 ppm in solution) extracted in carbon tetrachloride or isoamyl acetate. This highly specific method is commonly used in our laboratories for determining traces of Mo in all types of products (earth - fertilisers - ores - steels - refractory metals, etc.,).

The conventional thiocyanate method is also sensitive and relatively specific (17), but its sensitivity to Pt makes it impossible to make the solution in a Pt crucible and the instability of thiocyanate adds to the difficulty of the method. Other spectro-photometric processes are generally much less sensitive and/or less specific, particularly the following :

- a) Ophenanthroline and α α' dipyridyl are sensitive to Cu-Co-Al-Cr-Fe, etc., and are limited to 0.25 ppm in solution.

- b) Polyhydric phenols (catechol-pyrogallol-Tiron, etc.,) are sensitive to Fe^{3+} - Cu^{++} - W - U - V - Ti, etc., and sensitivity is limited to about 0.2 ppm in solution. Moreover, the instability of these products in air makes these methods fairly difficult.
- c) Oxine and substituted oxines such as 8-hydroxyquinoline-5-sulphonic acid cannot be applied, particularly in the presence of Fe - V, etc., and sensitivity is limited to 1 ppm in solution. However, a new process eliminates interference from iron by operating in the presence of fluorides (19).
- d) Unithiol (sodium 2,3 dimercapto propanesulphonate), fairly similar to dithiol, gives a very specific reaction although its sensitivity seems limited to 1 ppm in solution (16).
- e) The methods using hydrogen peroxide, trion (Sodium 1,2-dihydroxy 3-benzene 5-disulphonate), mercaptoacetic acid and 3 hydroxy 1, p-phenylsulphonate 3-phenyl triazene are particularly low in specificity and of limited sensitivity.
- f) The quercetin method may be made almost specific by a prior separation with F^{Ox} -benzoin oxime and chloroform, but W and V always give trouble.

DETERMINATION OF VANADIUM

Although this element can also be determined by conventional polarography without great difficulty, and by flame emission, spectro-photometric methods seem to provide the simplest course in this case.

We usually use oxinate spectro-photometry after selective extraction at a convenient pH factor by means of chloroform; interference from molybdenum, titanium and iron in particular, is eliminated by taking a measurement at two different wave lengths : vanadium oxinate is, in fact, the

only red-coloured oxinate in this solvent. It is obtained from either V^{4+} or V^{5+} .

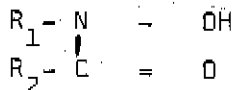
The sensitivity limit is of the order of 0.2 ppm in solution, so that 5 ppm is reached without difficulty in the case of the product (fertiliser or soil).


This method is unreliable, however, if the Fe/V ratio is very high (> 100 for example), as it then becomes clearly imprecise. It is still possible to decrease the working limit by adding a high concentration of alkaline fluoride which complexes the interfering element.

An aqueous colorimetric method was developed in 1959 (20), using pyrocatechol; it is slightly less sensitive as there is no concentration by extraction (limit of 0.5 ppm in solution, i.e., 50 ppm on the product analysed). However, this method unfortunately entails the use of cyanide as the agent for complexing possible interference.

The conventional heteropolyacid methods (phosphovanadotungstic and vanadotungstic) are lacking in specificity and require laborious separations beforehand, the simplest of which consists of at least one electrolysis on a mercury cathode. Indeed, the extraction of these complexes by ketones has still to be improved if sufficient precision is to be obtained.

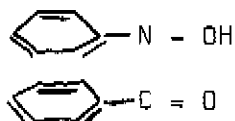
The newest methods involve the use of more or less substituted hydroxamic acids :



One of the simplest of this type of reagents, benzohydroxamic acid (BHA) $H-N-OH$ enables 0.2 ppm to be determined in  solution in hexanol (Fe-U-Ti and Sn interference being eliminated by washing the extract with a phosphate solution (21) or 0.5 ppm to be determined after a more selective extraction with deisobutylketone, which does not extract Fe-U-Ti (22).

However, it should be noted that these reagents are sensitive only to the vanadate ion, which means that vanadium must first be oxidized by adding a low concentration of bichromate.

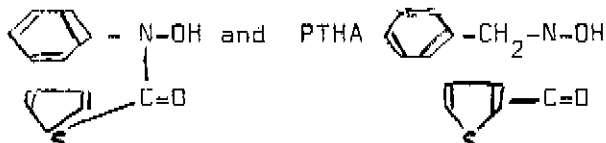
More highly substituted hydroxamic acids often remove the need for washing the extract, owing to their greater selectivity, and offer greater sensitivity as extraction may be performed with a non-polar solvent such as chloroform : these include N Benzoyl N Phenylhydroxy-



amine, which are less sensitive to iron interference and afford a sensitivity of the order of 0.1 ppm in CHCl_3 solution.

However, these advantages are compensated by lower stability of the reagent, particularly upon oxidation. Thus, the most complex molecules

of pTHA



are sensitive to dichromate which can then no longer be used to oxidize V^{4+} .

DETERMINATION OF SELENIUM -

Although no conclusive action has thus far been demonstrated in the vegetable field, the important part played by this element in the growth of animals has recently led to its being added to the list of more standard trace-elements.

The problem of its determination is relatively little known, yet it offers very good prospects both as regards sensitivity and precision, not to mention its specificity. At the present time, piazoselenol formation by reaction with aromatic orthodiamines is by far the best method of determining traces of this element.

3,3'-diaminobenzidine is the most commonly used reagent; after extraction by toluene, it enables one to attain a limit in solution of 0.1 ppm by absorption spectrophotometry and of less than 0.01 ppm by measuring the spectrofluorescence (23).

Rare interference from cations may be practically

eliminated by the use of EDTA (complexon) and the possible addition of ammonium chloride removes interference from high contents of sulphate.

As this method is specific, we use it in absorption spectrophotometry for determining Se to within a few ppm in metals and chromium in particular.

Even greater sensitivity (0.001 ppm and less with fluorescence) can be obtained by using 2,3 diaminonaphthalene (24).

DETERMINATION OF W -

This element was the last to be added to the list of trace-elements and its importance is still a matter for discussion.

The problem of determining it in trace amounts has already arisen in our laboratories in the field of pure metals (Niobium) and nuclearly pure products. Although we have scarcely had an opportunity of practical application ourselves in the case of fertilisers and soils, the specificity of the method we use enables us to recommend it without risk of undue difficulty.

Like Molybdenum, Tungsten gives with dithiol a highly coloured complex which may be extracted with carbon tetrachloride; however, the extract is a much more bluish green and the reaction takes place only in a sufficiently diluted acid medium ($\text{SO}_4\text{H}_2 \leftarrow 3\text{N}$). Moreover, it requires the prior reduction of W to the W^{5+} state. It is a simple matter to effect this reduction by means of a titanous chloride solution.

In practice, Molybdenum is firstly determined in a moderately acid medium; after this element has been extracted, the aqueous layer is concentrated, reduced by adding TiCl_3 and hydrochloric acid under heat and, finally, the Tungsten is extracted by CCl_4 after a fresh addition of dithiol and a suitable dilution.

Specificity is excellent, with sensitivity of the order of 0.1 ppm in solution.

A similar method has since been published by HOBART & HURLEY (25).

The traditional method using thiocyanate is found to be

less sensitive and, more important, less selective and far less precise owing to the low stability of the complex and more or less well-defined interaction with numerous ions.

Other possible reagents are even less sensitive and not even as precise.

Flame emission or absorption cannot be used with sufficient sensitivity, at least in the case of the butane/air flame, although in a tartaric acid medium polarography affords a limit of sensitivity of the order of 0.2 ppm in solution.

CONCLUSIONS

The precise determination of trace-elements presents hardly any very difficult problems at the present time; three types of methods in particular may be used after the soil or fertiliser being analysed has been placed in solution.

The most general method is spectro-photometry; for this one must have a precision spectro-photometer with a fairly wide wave-length band; such equipment is available at prices in the order of 5,000 Francs. However, these processes require a minimum of manipulations (usually extraction by solvent) which may add to the cost price.

The polarographic method affords an appreciable saving in time if a recording polarograph is used, but this equipment is double the cost of the preceding type and difficulties must be expected in the case of determining molybdenum and selenium and, finally, it is practically impossible to determine boron.

Finally, the flame emission and absorption techniques are extremely fast and thus enable the cost of analysis to be greatly reduced if the latter's output enables the equipment to be written off at an acceptable rate. This equipment is four times more expensive than the simple spectro-photometer mentioned above. However,

this technique does not afford very sensitive determinations of selenium, boron or cobalt.

We maintain that it is possible to deal with all problems concerning trace-elements with equipment representing a fairly low amortisation cost, and that great possibilities are thus open to agronomists to improve our knowledge in this sphere.

However, we must point out that we have tackled only the determination of elements after they have been placed in solution, and intentionally ignored the state in which they are found in the product to be examined and their actual assimilability. Although there is no special analytical problem involved in determining the total strength, the speed of action of the principal fertilising elements has still to be determined. So far, little study has been made of this problem (26) which, to be overcome, will require close collaboration between chemists and agronomists.

We would point out from the start that a distinction should be made between, at least, the total content, the content soluble in water and, probably for want of anything better, the content soluble in one or more of the more or less conventional reagents.

The first two forms are being checked as a matter of course, particularly in the United States, not only in soils but also in fertiliser products that are devised specially to prevent any undue immediate solubility which might poison the crops. Such a requirement restricts the use, on an industrial scale, of products that are very rich in trace-elements.

From this point of view, it is far better to supply these within fertilisers in which they are highly diluted.

This may be the case with superphosphates when the trace-element is added to the acid used for the solubilisation of phosphate rock, but in fact is always unavoidably the case owing to the appreciable amounts of B-Mo-Cu-Mn-Zn-Co-Se-V, etc., in the original phosphates.

We would emphasise that there is good reason to believe

that these traces are in a relatively assimilable form and that, as may be seen from the following analyses, the amounts contained are finally at least as great as in organic substances that are considered to be of particular interest from this point of view.

ppm of	B	Mo	Cu	Mn	Zn	Co	V	Se
(Lucerne Compost	70	2	42	260		0.11		
Peat Compost	13	2.1	7	110	20	0.02		
* Corn straw Compost	15	0.5	8	47	32	0.02		
(Maize stalk Compost	15	0.4	12	25	66			
U. S. Phosphates	15	3	20	600	40			1
average figure	to 20	to 4	to 30	to 700	to 50		150	to 2
North African Phosphates			100	very low 1 ppm	100 to 200		50	
18% Superphosphate (Moroccan phosphate)					180		40	

To sum up, it would appear to be in the interests of superphosphate manufacturers to periodically check the strength of trace-elements in their products, as the presence of these may in future prove to be of much greater interest when compared to fertilisers with higher concentrations of P, N and K.

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