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STUDY OF THE ESTIMATION OF CERTAIN TRACE IMPURITIES BY FLUORIMETRIC METHODS

FINAL TECHNICAL REPORT

by

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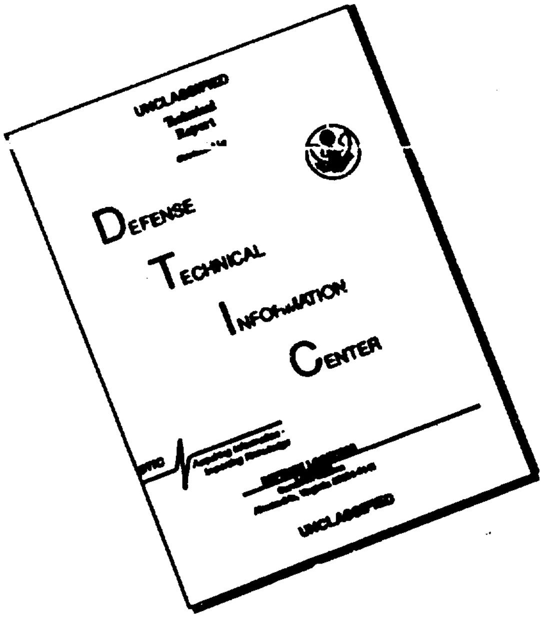
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ABSTRACT

Work carried out during the fourth year of the present contract is reported.

The preparation and development of a new fluorimetric reagent for magnesium is described. This is N.N'-bis salicylidene-2,3-diaminobenzofuran. The spectral characteristics of the magnesium complex are given together with evidence to show that this is the most sensitive magnesium reagent so far tested in this programme.

Details are given of work on the development of separation techniques for the removal of microgram quantities of magnesium from gram quantities of molybdenum and nickel. Full experimental data is presented concerning a new method for the determination of up to 2 p.p.m. magnesium in nickel.

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1. INTRODUCTION

The research described in this report was carried out during the fourth year of the present contract. The object of the work being to develop analytical methods for the fluorimetric determination of traces of aluminium, magnesium and silicon in nickel, titanium, niobium, tantalum, molybdenum, tungsten, rhenium and some compound semiconductor materials.

At the beginning of the period under review, considerable progress had been made with several aspects of the programme. A literature survey had revealed that a large number of possible fluorimetric reagents existed for aluminium and magnesium. A number of these had been selected for further investigation, prepared where necessary, and purified. We had established, the optimum reaction conditions for each reagent and had worked out analytical procedures based on these for aluminium and magnesium.

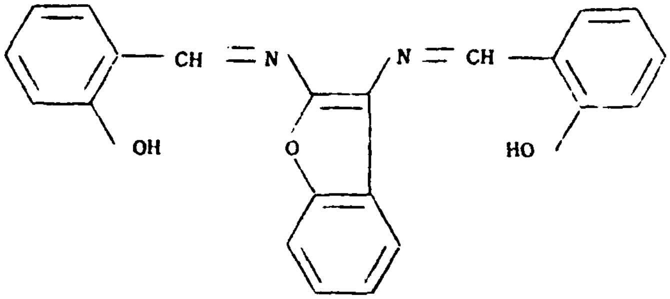
Simultaneously with this work on reagents, an instrument had been developed which measured the absolute excitation and fluorescence spectra of metal chelates. This had been used to provide true spectral data for each metal/reagent complex, enabling an accurate comparison of reagent sensitivities to be made.

At the beginning of this year, we were thus in a position to review the characteristics of the various fluorimetric reagents examined and to select the most suitable for our applications. This year's effort has been concentrated mainly on the investigation of methods for the separation of submicrogram quantities of aluminium and magnesium from gram quantities of matrix materials.

In addition one further fluorimetric reagent has been examined, characterised and shown to be the most sensitive reagent so far examined.

2. FLUORIMETRIC REAGENTS

The new fluorimetric reagent studied this year is N.N'-bis-salicylidene-2,3-diaminobenzofuran (S.A.B.F.)



The fact that this compound forms a fluorescent complex with magnesium ions was first reported by Smith(1), who claimed that the reagent was very sensitive and specific for the determination of magnesium and gallium. The specificity was attributed to the fact that the molecule acts as a rigid cage into which only chelated metal ions of radius less than 1Å can be fitted.

It appeared that this reagent would be extremely useful since it is very sensitive and its magnesium complex can be extracted into iso-butylmethylketone (I.B.M.K.) from aqueous solution. This provides a concentration step which is particularly advantageous in this type of work. None of the magnesium reagents we had studied previously gave extractable complexes. A sample of S.A.B.F. was, therefore, prepared and its reaction with magnesium studied.

2.1 Preparation of S.A.B.F.

The following procedure was used forthe preparation of the reagent:-

A mixture of 50 ml. salicylaldehyde and 80 ml. ethanol were de-aerated by a stream of nitrogen for 20 minutes, 15 ml. of ammonium hydroxide (S.g.0.88) were added and the beaker placed in an ice-bath. When cold, a solution of 6 g. potassium cyanide in 9 ml. water was added to the mixture with vigorous stirring. After 2 hours the resulting solid mass was broken up, 50 ml. ethanol and 15 ml. ammonium hydroxide added and the mixture stirred for 2 hours in the ice-bath. The product was then filtered and washed well with 50% aqueous methanol, followed by pure methanol until the washings were clear yellow in colour. The orange-yellow solid was dried in a vacuum dessicator over calcium chloride and recrystallised from a mixture of dioxan and water. (Melting point 181°C.)

The reagent was used as a 0.02% solution in A.R. dioxan and was prepared fresh each day.

2.2 Experiments to Determine the Optimum Conditions for the Mg/S.A.B.F. Reaction

The original publication concerning this reagent was very brief and gave little experimental detail. Subsequently the full paper was published by Smith et al.(2) In the interim period we conducted experiments to ascertain the optimum conditions for the reaction to investigate possible interference with the method, and to establish the spectral characteristics of the Mg/S.A.B.F. complex. It was decided to investigate the solvent extraction procedure briefly discussed by Smith(1), since this offered the chance of a concentration step during the procedure and the opportunity to use masking agents to retain interfering elements in the aqueous phase.

According to Smith(1), magnesium could be determined fluorimetrically by developing the Mg/S.A.B.F. complex in aqueous solution buffered to a pH of 12.4 with a (2:1) solution by volume of pyridine (Py) and diethylamine (Et_2NH). After extraction from the aqueous phase with iso-butylmethylketone (I.B.M.K.), the fluorescence intensity of the complex was measured. The excitation and fluorescence maxima for the complex were stated to be at a wavelength of 475 n.m. and 545 n.m. respectively.

It was reported that at pH values of 10-12, only partial extraction of the complex occurred, this was the cause of low results. In the absence of pyridine, the Mg/S.A.B.F. could not be extracted by organic solvents. The mechanism suggested was the replacement of water molecules in the Mg/S.A.B.F. co-ordination sphere by pyridine molecules. This was confirmed in a later paper by West(2) who showed that magnesium and S.A.B.F. form a 1:1 complex with the structure $Mg/(H_2O)_2(S.A.B.F.)$. The hydrated complex was only slightly soluble in pyridine, diethylamine, dimethylsulphoxide, dioxan and insoluble in organic solvents such as chloroform, carbon tetrachloride, aromatic and aliphatic solvents. Pyridine molecules when present in solution replace the co-ordinated water molecules in the complex rendering it soluble in solvents such as I.B.M.K.

According to Smith, diethylamine acts only as a strong base.

2.2.1. To find the Optimum pH for the Fluorimetric Determination of Magnesium Using S.A.B.F.

A series of solutions was prepared containing 2 µg Mg., 1 ml. 1% aqueous KCN (to complex interfering ions) and 3 ml. of (2:1) pyridine/diethylamine buffer solution. Using 10% HCl or Et_2NH, the pH of the solutions were adjusted to 12.1, 12.2, 12.3 etc. to 12.6 and 2 ml. of 0.02% S.A.B.F. in dioxan added. The Mg/S.A.B.F. complex was then extracted with two 10 ml. portions of I.B.M.K. The volume of the extract was made to 25 ml. with I.B.M.K. The fluorescence intensity of the solution was measured after the addition of a little anhydrous sodium sulphate to absorb any water present. Previously this had been achieved by making the volume of the extract to 25 ml. with absolute ethyl alcohol. On a number of occasions, however, after this solution had stood for a few minutes a white turbidity developed which prevented the measurement of the fluorescence.

We found that maximum fluorescence occurred at a pH of 12.3 (Fig.2) decreasing rapidly at higher values. The reason for this was the appreciable increase in the concentration of Et_2NH (sometimes up to 5 ml.) required to give pH values in excess of 12.3. This increased the mutual miscibility of the aqueous and I.B.M.K. phases resulting in a reduction in the proportion of the complex extracted and low results. In order to obtain a pH of 12.6, the volume of Et_2NH added was so large that it causes the two phases to become completely miscible.

2.2.2. To Study the Effect of Pyridine Concentration on the Fluorescence Intensity of the Mg/S.A.B.F. Complex

In this series of experiments varying quantities of pyridine were added to a number of test solutions, to study the effect that this had upon the efficiency of extraction of the Mg/S.A.B.F. complex. In order that these variations should effect only the mutual solubility of the aqueous and I.B.M.K. phases and not the pH, a borate/sodium hydroxide mixture was used to buffer the solution. [10g. sodium borate decahydrate and 10g. sodium hydroxide per 100 ml. H_2O]. An inorganic buffer was chosen in order to limit the number of components extracted by the solvent to, S.A.B.F., Mg/S.A.B.F., pyridine and diethylamine.

To a series of solutions containing 2 µg Mg. and 1 ml. 1% aqueous KCN were added volumes of pyridine in the range shown by Fig.3, followed by a 1 ml. addition of borate/hydroxide buffer.

2 ml. 0.02% S.A.B.F. in dioxan was then added and the pH adjusted to 11.9 with 10% solution of NaOH or HCl, this being the pH at which maximum fluorescence occurs under these conditions. (Fig.2).

The fluorescence of the Mg/.S.A.B.F. solution was measured after extraction from the aqueous phase by I.B.M.K. as in Section 2.2.1.

This series of experiments showed that 2.0 ml. pyridine gave maximum fluorescence of the complex (Fig.3). Above this the intensity remained substantially constant.

2.2.3. To Study the Effect of Diethylamine Concentration on the Fluorescence of the Mg/S.A.B.F. Complex

The pH of a series of solutions containing 2 µg Mg, 1 ml. 1% KCN, 2.5 ml. pyridine, 1 ml. borate/hydroxide buffer and 2 ml. 0.02% S.A.B.F. in dioxan, was adjusted to 11.90 with 10% NaOH or HCl.

The Mg/S.A.B.F. complex was extracted by two 10 ml. portions of I.B.M.K., a series of volume additions of diethylamine was added as shown by Fig.5. The final volume of the extract made to 25 ml. with I.B.M.K. and the fluorescence intensity measured.

From previous tests it had been noticed that most of the diethylamine added to the aqueous phase was extracted by the I.B.M.K. It was possible therefore for interference to occur in two ways:

(a) by increasing the miscibility of the I.B.M.K. in the aqueous phase and reducing the efficiency of extraction of the Mg/S.A.B.F. complex,

(b) by extraction into the organic phase where it could cause inner filter effects which reduce the fluorescence intensity measured.

To investigate (b), the additions of diethylamine were made to the Mg/S.A.B.F. extract as described above.

Results (Fig 5A), showed a rapid rise in fluorescence intensity in the range 0.0 to 1.0 ml. additions of diethylamine, levelling almost to a plateau in the range 1.0-2.0 ml. having a maximum at 1.5 ml. Et_2NH. At additions of greater than 2.0 -3.0 ml., the intensity began to decrease. The experiment was repeated and a curve obtained (Fig.5B) having a more pronounced maximum at a point corresponding to an addition of 1.4 ml. Et_2NH

It appears therefore that the Et$_2$NH plays an important part in the procedure, in addition to adjusting the "pH" of the solution. Up to 1.5 ml. Et$_2$NH/25 ml. I.B.M.K. enhance the fluorescence of the Mg/S.A.B.F. complex but greater additions reduce it.

The mechanism of the effects proposed is not know, and although further investigation would prove interesting, it was not considered necessary in connection with this work.

The preceeding experiments show that the maximum fluorescence of the Mg/S.A.B.F. complex was obtained when it was developed in aqueous solutions in the presence of 2.5 ml. pyridine buffered to a pH of 11.9 with a borate/hydroxide buffer, 10% solutions of NaOH or HCl being used to adjust the pH as necessary. Extraction of the complex with I.B.M.K. and addition of 1.5 ml. Et$_2$NH before making the volume to 25 ml. with I.B.M.K. completes the procedure.

2.2.4 Calibration of the Method for the Fluorimetric Determination of Mg Using the S.A.B.F. Reagent

A series of solutions were prepared consisting of 40 mls. distilled water, 0, 1, 2, 3, 4, 5 µg Mg. respectively, 1 ml. 1% aqueous KCN, 2.5 ml. pyridine, 1 ml. borate/hydroxide buffer and 2 ml. 0.02% S.A.B.F. in dioxan.

The pH of each solution was adjusted to 11.9 with 10% NaOH or HCl and the Mg/S.A.B.F. complex extracted by two 10 ml. portions of I.B.M.K. To this was added 1.5 ml. Et$_2$NH and the total volume made to 25 ml. with I.B.M.K. The extracts were clarified by the addition of anhydrous sodium sulphate to remove water dissolved in the I.B.M.K. before reading the fluorescence intensity.

The graph obtained (Fig.6) was linear in the region 0 - 2.0 µg Mg. and again between 2.0 and 5.0 µg Mg a change of slope occurring at the 2.0 µg point.

We were unable to account for this change in slope, but suspected the sodium hydroxide used for the pH adjustment to be responsible. The calibration was therefore repeated, adding the Py/Et$_2$NH buffer and using Et$_2$NH to adjust the pH to 12.3 instead of 10% NaOH.

A reproducible linear graph was obtained (Fig.1), enabling 0.10-5.0 µg Mg to be determined. This method was therefore considered to be satisfactory.

2.2.5 The Determination of the Spectra and the Sensitivity of the Mg/S.A.B.F. Complex

The true spectral characteristics of the Mg/S.A.B.F. complex were determined with the spectro fluorimeter using exactly the same instrument configuration, conditions and procedure as were employed in our previous work of this type(10)

The excitation spectrum obtained in this way was a true spectrum, i.e it was independent of all instrument characteristics. The fluorescence spectrum, as measured, was not a true spectrum and was corrected in the way described in our last report(10).

The true spectra so obtained are shown in Fig. 9. The peaks of the main excitation and fluorescence bands occur at 2.03 μ^{-1} (493 n.m.) and 1.61 μ^{-1} (620 n.m.) respectively. These values may be compared with those of West et. al(2) for uncorrected spectra, of 525 n.m. and 555 n.m. respectively.

The sensitivity of the S.A.B.F. reagent was also determined in exactly the manner described in our previous report (10 page 31 et. seq.) considerable care being taken to reproduce the experimental conditions used previously. As before, the results were compared directly with those obtained from a standard quinine bisulphate solution. This enables comparisons to be made between the sensitivity values of different reagents obtained at different times. In our previous report(10), the sensitivity results were tabulated (Table 3), together with all the necessary data for correction of measured values for instrument variables. The results for the S.A.B.F./Mg complex are given in an identical manner.

Fluorescing Species	Q.SO$_4$	Mg/.S.A.B.F.
Calibration Range p.p.m.	1 - 10	0.04 - 0.2
Calibration Slope	0.83 x 25	0.78 x 25
Final vol of Soln. ml.		25.0
Uranium Glass Balance	4.5 x 25	4.35 x 25
Volume Correction - Multiply	½	1
Uranium Glass Correction - Multiply	1	1.04
Fluorescence Spectrometer Correction - Divide	1.96	0.27
Total Correction - Multiply	0.51	3.85
Corrected Slope	10.5	15.0
Sensitivity Index		0.70

The value of 0.70 for the Sensitivity Index makes this the most sensitive magnesium reagent tested in this programme.

2.2.6. A Study of Elements Causing Interference with the Fluorimetric Determination of Magnesium as the Mg/S.A.B.F. Complex

Smith(1) and West(2) report that many metals with ionic radii less than 1Å react with S.A.B.F. A study of ionic radii(9) shows that many elements commonly encountered in analytical chemistry come in this category. West(2) reports that in 100-fold molar excess over magnesium, the following ions do not interfere with the method.

Al^{3+} Hg^{+} Mn^{2+} Pb^{2+} Sb^{3+} Sb^{5+} As^{3+} As^{5+} Ba^{2+} Be^{2+} $Bo3^{3-}$ Cr^{6+}

Ga^{2+} Ge^{4+} Hg^{2+} K^{+} Mo^{6+} Na^{+} Sr^{2+} Ti^{4+} Te^{+} V^{5+}

Acetate, bromide, chloride, cyanide, fluoride, iodide, nitrate, perchlorate, sulphate, sulphide.

The following cause interference by

(a) Formation of a coloured non-fluorescent complex with S.A.B.F.

Ca^{2+} Cd^{2+} Co^{2+} Cr^{3+} Cu^{2+} Fe^{2+} Fe^{3+} Mn^{2+} Ni^{2+} Pd^{2+} Zn^{2+}

(b) Formation of precipitates with Cl^{-} or OH^{-} on which the magnesium co-precipitates or adsorbs as the Mg/S.A.B.F. complex.

Ag^{+} Hg^{+} Pb^{2+} Sr^{2+} Sn^{4+} Th^{2+} Zr^{4+}

Although the following ions do not precipitate or give coloured complex with S.A.B.F., they do interfere, probably by displacing the magnesium from the Mg/S.A.B.F. complex to give a non-fluorescent colourless compound.

They are:

Bi^{2+} In^{3+} La^{3+} Sb^{3+} Se^{4+} Te^{4+} Y^{3+}

Phosphate, nitrate, tartrate and complexones such as E.D.T.A. destroy the fluorescence by forming a more stable complex with magnesium than the S.A.B.F. reagent.

The foregoing information was of interest but could not be applied directly to our investigation where the matrix material would be present in approximately 4 x 10^5 fold molar excess. We therefore selected for investigation specific interferences which were relevant to the methods being developed.

2.2.6.1. Cyanide.

The effect of cyanide on the development of the Mg/S.A.B.F. complex was investigated with a view to using it to complex ions which interfere with the method. It was found that a 6×10^3 fold molar excess did not interfere, and it is possible that an even larger excess can be tolerated. However, in an attempt to develop the Mg/.S.A.B.F. complex in aqueous solution containing nickel complexed with a 10^6 molar excess of cyanide, interference did occur giving low recoveries of magnesium. It was concluded that addition of cyanide up to 6×10^3 fold molar excess, prior to the development of the Mg/S.A.B.F. appeared to be a satisfactory method of preventing interference from ions which form soluble complex cyanides.

2.2.6.2. Molybdenum.

Experiments showed that up to 250 µg of molybdenum had negligible effect on the method of the determination of magnesium, while in the presence of cyanide, up to 500 µg could be tolerated.

2.2.6.3. Nickel.

In the presence of cyanide, up to 1,000 µg of nickel caused no interference.

2.2.6.4. Aluminium.

Up to 250 µg of aluminium could be tolerated but interference occurred at the 500 µg level.

2.2.6.5. Calcium.

In experiments to establish separation procedures for magnesium from matrix materials, calcium was found as a contaminant. Greater than 10 µg caused interference by the formation of a red-coloured, non-fluorescent complex with S.A.B.F. This caused low values of the measured Mg/S.A.B.F. fluorescence intensity.

The use of Sr/E.D.T.A. (0.1M. Sr + 0.1M E.D.T.A. in the ratio 2:1/by volume) recommended by West(2), to complex the calcium was found to be successful when the calcium concentration was known and an exactly equivalent amount added. When present in excess of that required to complex the calcium, the Sr/E.D.T.A. solution caused a reduction in fluorescence of the Mg/S.A.B.F. This effect can be explained by a study of the stability constants concerned(7). This shows that the magnesium and strontium E.D.TA. complexes have approximately equal stability constants, as a result an interchange occurs between Mg^{2+} ions in solution and Sr^{2+} ions held by the E.D.T.A. giving a reduction in the Mg/S.A.B.F. formed.

COMPLEX	Log K
Mg/EDTA	8.69
Sr/EDTA	8.70
Ca/EDTA	10.70

The use of oxalate to complex calcium was unsuccessful because magnesium is complexed more strongly by oxalate than by S.A.B.F., preventing the formation of the Mg/S.A.B.F. complex.

COMPLEX	Log K
Mg/oxalate	2.55
Mg/SABF	<1.36
Ca/oxalate	3.00

3. SEPARATION TECHNIQUES

3.1 Introduction

Work on separation techniques has been concentrated on an ion-exchange procedure for the removal of molybdenum, while mercury cathode electrolysis and solvent extraction procedures have been investigated for the removal of nickel.

3.2 Experiments on the Separation of Magnesium from Molybdenum

3.2.1. We have previously (3) carried out experiments on the separation of molybdenum from traces of aluminium and magnesium using an ion-exchange from HF/HCl solutions. While this system resulted in an effective separation, it unfortunately gave rise to high and variable process blanks, even when a long and meticulous column purification procedure was used. After various attempts at improving the method had been unsuccessful, it was discarded in favour of an ion-exchange procedure based on work by Spano and Green (4). These workers have developed a method for the separation and determination of "trace" impurities from gram quantities of molybdenum using ion-exchange followed by X-ray spectrography. Magnesium and aluminium were determined more or less successfully at the 30 µg level, although process blanks were somewhat variable especially in the case of aluminium. The lack of precision of aluminium determinations was attributed by the authors to the variable distribution of this element through the cross-section of the paper discs used as X-ray targets and to the absorption of the long wavelength K_α radiation of aluminium by the disc material. Since we were intending to use a fluorimetric finish it was clear that these particular difficulties would not arise in our procedure.

The Spano and Green ion-exchange separation technique was seen to have several advantages over those which we had used previously:-

(i) Since it was a cation exchange procedure, only a small resin column would be required to take up the trace constituents as cations, while the major constituent would be washed through as the molybdate ion. The use of a much smaller resin bed should considerably reduce the contribution made to the blank by the ion-exchange material.

(ii) The separation process was carried out in hydrochloric acid solutions, therefore the use of glass apparatus was not prohibited, as when hydrofluoric acid mixtures were used in our previous method.

(iii) The same column of resin could be re-used, eliminating the need for repeated purification of fresh column material.

3.2.2 Reagents

The Spano and Green method called for a strong cation exchange resin similar to Dowex 50WX12, we therefore used 220 mesh Zeo Karb 225 X 9. in the hydrogen form. A resin column 1.5 cm. in diameter by 10 cm. high was used, initially this was pretreated in the standard way by eluting with 20 column volumes of 6N hydrochloric acid, at a flow rate of 0.5 ml. per minute. Later it was found necessary to use more rigorous purification methods; these will be described below.

Measurements of the final magnesium concentrations were carried out fluorimetrically using the S.A.B.F. reagent described above. It was quickly found that the Analar grade of hydrochloric acid used contained sufficient magnesium and calcium to seriously upset the method. The 70 ml. of 6N. HCl used as eluant were found to contain as much as 2-3 µg magnesium and 40 µg calcium. Purification of the acid was effected by distillation in a quartz apparatus; the strength of the azeotropic mixture distilled was estimated and a suitable dilution carried out to give the required acid concentration. This purification reduced the level of both magnesium and calcium in the eluting acid to less than 0.5 µg/ml.

3.2.3. Experimental

3.2.3.1. Initial experiments were carried out to assess the degree of completeness of separation of molybdenum from magnesium by the Spano and Green procedure. To this end, pure molybdenum (2.0 g.) and pure magnesium (10.0 µg) solutions were taken separately through the procedure and these elements estimated in the final 6N HCl eluate.

3.2.3.2 Molybdenum

Molybdenum solutions were prepared by dissolving 2.0 g of the powdered metal (99.99% pure) in $H_3PO_4/HNO_3/H_2O_2$, according to the Apano and Green procedure. After dissolution and appropriate evaporation, the solution was diluted to 75 ml. with water and passed through a Zeo-Karb 225 ion-exchange column prepared as described above (Section 3.2.2.). The eluate was discarded and the column was washed by passing down it 50 ml. of 0.5N HCl solution at a flow rate of 1 ml./minute - the eluate was discarded. Finally, 75 ml. of 6N HCl was passed through the column at a rate of 0.65 ml. per minute and the eluate retained for molybdenum estimation. After evaporation of the eluate solution almost to dryness, it was diluted to 50.0 ml. and an aliquot taken for the determination of molybdenum by the thioglycollic acid procedure of Will and Yoe(5).

The results of this investigation were somewhat suprising, since they showed that a considerable proportion of the molybdenum was retained by the column, in spite of the 0.5N HCl wash, and was subsequently eluted by the 6N HCl. Molybdenum residues of 1.0 mg. or more were common at this stage of the investigation. It had already been shown that the magnesium/S.A.B.F. procedure could not tolerate molybdenum concentrations greater than 500 µg/75 ml. of eluate, so some means of improving the separation had to be sought.

The most likely explanation for the partial retention of the molybdenum by the cation exchange column, was that a proportion of it was present, not as molybdate ions, but as cations formed by reduction of molybdate ions. These unwanted cations would be adsorbed by the resin at the first stage and subsequently eluted only by 6N HCl. Attempts to overcome this were made by incorporating hydrogen peroxide into the 0.5N HCl wash, in order to reoxidise adsorbed molybdenum to the 6-valent state and so to remove it from the column. The use of strong peroxide solutions at this stage was not possible, since they caused considerable effervescence and subsequent channelling of the resin bed. On the other hand, weak peroxide solutions did not efficiently remove the molybdenum from the column. A compromise solution was therefore adopted, in which a relatively weak peroxide wash solution (0.5N HCl 1% with respect to H_2O_2) was used. This removed molybdenum sufficiently to reduce the residue to below the tolerance limit of the S.A.B.F. method, while not causing undue disturbance of the column.

In this way the quantity of molybdenum remaining in the 6N HCl eluate from an intial sample of 2.0 g. was kept to 200 µg.

3.2.3.3. Magnesium

A similar procedure to that described above was used to investigate the recovery of 10.0 µg quantities of magnesium by the Spano and Green procedure. 75 ml. sample solutions containing magnesium H_3PO_4, H_2O_2 and HNO_3 in the correct proportions were passed through a cation-exchange column, the column washed with $H_2O_2/0.5N$ HCl and finally eluted with 6N HCl.

Magnesium was estimated in the eluate after careful evaporation to dryness, the S.A.B.F. fluorescence method described in Section 2.2.4. being used. Results showed that only a small proportion of the magnesium added was recovered after the separation, the remainder was presumed to be held back on the column in some way.

It was shown later that the low recoveries were due partly to interference by calcium impurities eluted from the column, although this did not account for the situation completely.

It was therefore decided that this loss of magnesium should be investigated using a radioactive isotope, Mg^{28}, since this would allow easy tracing of all the magnesium ions.

3.2.3.3.1. Experiments with Mg^{28} tracer

Magnesium -28 is the only readily available radioactive isotope of magnesium for use in tracer work, although it it not a particularly convenient isotope to use, since it has a fairly short half-life (21.3 hours). It decays by β-emission via aluminium -28 to the stable isotope silicon 28:-

$$Mg^{28} \xrightarrow[21.3\ \text{hrs}]{\beta} Al^{28} \xrightarrow[2.3\ \text{mins}]{\beta} Si^{28}$$

It was found most convenient to count the associated gamma radiation of the aluminium -28 daughter element in equilibrium with the magnesium -28, using a single channel gamma-spectrometer. The energy peak occurred at 1.78 MeV. The isotope used was available at a specific activity of 1 Ci/g. Experiments were performed with 3 µCi aliquots of the isotope solution diluted with 7µg inactive magnesium carrier, which gave a total magnesium concentration of 10 µg in each case.

Three experiments were carried out with this radioactive tracer. In the first, 10 µg magnesium in a volume of 75 ml. water was run onto a Zeo-Karb 225 ion-exchange column prepared as described above, the eluate was collected in three 25 ml. portions, evaporated just to dryness and any gamma-activity counted on the gamma spectrometer. The column was then washed with 50 ml. 0.5N HCl (1% with respect to hydrogen peroxide) the eluant being collected in 10 ml. portions and the gamma-activity counted. Finally, the magnesium was eluted from the column with 75 ml. 6N HCl at a rate of 1.0 ml. per minute and collected in 5.0 ml. portions for counting.

Figure 10 (Experiment I) shows the results obtained from this experiment. It indicates that the magnesium was quantitatively retained by the ion-exchange column during both the addition of the sample and the subsequent washing with 0.5N HCl. Magnesium was eluted rapidly by 6N HCl, elution being complete after the passage of 35 ml. of eluant. A summation of the counting rates for all the 6N HCl fractions gave a figure for the total quantity of magnesium eluted from the column. This, compared with the count rate of a prepared Mg-28 standard, indicated that only 86% of the magnesium added to the sample had been recovered. This figure confirmed those obtained earlier from non-active experiments and was lower than desired. By monitoring the ion-exchange column and reservoir with a Geiger-Müller type counter, it was found that the magnesium activity remaining on the column was spread in a diffuse manner throughout the apparatus. This suggested that the lost magnesium had been adsorbed onto the glass walls of the column-tube and reservoir, an explanation which is compatible with the small quantities of magnesium in question (1-2 µg Mg.)

We had successfully prevented losses of this type on previous occasions by treating the walls of the glass vessels, with a silicone fluid "Repelcote" (2% solution of dimethyldichlorosilane in carbon tetrachloride). The adsorbed layer of silicone on the glass prevents wetting by aqueous solutions and therefore adsorption of ions. Accordingly, the glassware used in these ion-exchange experiments was treated in this way, the column was repacked and the first tracer experiment repeated. The results, shown in Fig 10, (Experiment II), are identical with those of the previous experiment except that a much higher recovery of magnesium was attained (97%). This indicated that the adsorption theory was correct and that the steps takento overcome the defect had been successful; moreover, the presence of the silicone in the apparatus had no adverse effect on the operation of the ion-exchanger.

Both the above experiments had been performed in the absence of large quantities of molybdenum. A final test was therefore performed to investigate the effect, if any, of molybdate ions equivalent to 1.0 g. molybdenum on the elution of magnesium. Again, 10 µg of magnesium was used (7 µg $Mg^{natural}$ + 3 µg Mg^{28}) but to this was added a solution of 1.0 g molybdenum metal (99.99%) prepared by the method of Spano and Green(4). This solution was treated in the manner described above. The results are shown in Fig. 10 (Experiment III). From this diagram it can be seen that the magnesium was eluted by the 6N HCl more readily in the presence of molybdenum than in its absence. However, it is also apparent that the recovery of magnesium was somewhat lower in this experiment than in the previous one, although it was considered that a 92% recovery was adequate for these levels of determination, providing it was reproducible.

3.2.3.4 Having satisfied ourselves that the ion-exchange procedure gave a good separation of magnesium from molybdenum, the next step was to calibrate the method. This was attempted initially using pure magnesium solutions with no molybdenum additions. This series of experiments was unsuccessful due to the pick-up of both calcium and magnesium impurities from the ion-exchange resin. Calcium interferes with the development of the Mg/S.A.B.F. fluorescence as described above in Section 2.2.6. by complexing with S.A.B.F. to give a pink non-fluorescent compound. It was found possible to eliminate the calcium interference

interference/....

by pretreating the ion-exchange material with ammoniacal E.D.T.A. solution (pH 10.0). For reasons which are obscure, this did not remove the magnesium interference, although theory predicts that the resin should be effectively stripped of all magnesium impurities by this treatment. Blank determinations were carried out on the ion-exchange step of the procedure, followed by the development and measurement of Mg/S.A.B.F. fluorescence, using solutions containing no added magnesium or molybdenum. These gave results corresponding to quantities of magnesium varying between 0.2 and 2.0 μg Mg. Since the object of this project is to determine submicrogram quantities of magnesium, such a wide variation in blank-level is not permissible.

Attempts to improve this situation by column purification methods have met with little success, so that we have been forced to the conclusion that the ion-exchange procedure is not applicable to the determination of sub-microgram quantities of magnesium. If this is considered together with our previous experiences of this type of separation, it becomes apparent that until ion-exchange resins of greater purity become available, this type of process will always suffer from similar high blank problems.

3.3 Experiments on the Separation of Magnesium from Nickel

3.3.1. Electrodeposition of the Matrix Material at a Mercury Cathode.

Electrolysis from dilute sulphuric acid solution using a mercury cathode, offers a quick quantitative method for the separation of Mg, Al, Ti, Zr, P and V from Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Rh, Pd, Ag, Cd. In, Sn, Re, Ir, Pt, Au, Hg, Th and Bi. It also has the advantage of requiring the minimum of attention.

Using a modified form of the conventional Melaven cell (Fig.11), we were successful in removing (in 2 - 3 hours), all but a trace of nickel, (about 1 μg) from sample solution containing 1 gm Ni in 3M.H_2SO_4 spiked with 1 - 5 μg Mg. The nickel free sample solutions were then evaporated to dryness the residue taken up in water and the magnesium determined as in Section 2.2.4. We encountered serious difficulties, being unable to obtain reproducible sample or blank values. This was attributed to incomplete dissolution of the residue after evaporation of the H_2SO_4. Initially, the experiment was repeated and the residue taken into solution with a few

few/.....

drops of 6M hydrochloric acid, evaporated almost to dryness, diluted with distilled water and the magnesium determined as before. The results were still erratic. Both redistillation of the sulphuric and hydrochloric acids to remove impurities and conduction of the electrolysis in 0.3M instead of 3M.H_2SO_4 failed to produce better results. During the experiment it had been noticed that the addition of large volumes of Et_2NH were necessary to obtain a pH of 12.3 before developing the Mg/S.A.B.F. complex. It was shown (Section 2.3.3.) that more than 1.0 ml. Et_2NH reduced the fluorescence intensity of the Mg/S.A.B.F. complex. Varying concentrations of diethylamine required to neutralise the various concentrations of acid left after the evaporation stage would therefore account for the erratic results. The 1 µg Ni left in solution after electrolysis would not interfere as it had been complexed with cyanide.

A further experiment was performed in which, after the electrolytic removal of nickel, the pH of the acid solution was adjusted to approximately 4 with 10% NaOH and the magnesium then determined in the normal way.

A linear calibration graph was obtained in the range 0.0 - 2.0 µg magnesium.

Although this provided a method for the determination of 0.0 - 2.0 µg Mg in 1 gm. Ni, we hoped to be able to extend the range and considered alternative procedures.

3.4.

3.4.1. Investigation of Solvent Extraction Procedures for the Separation of Magnesium from Nickel.

We hoped to find a reagent which, after the sample had been brought into solution, would complex the nickel in the aqueous phase, leaving the magnesium uncomplexed. The Mg/S.A.B.F. complex would then be developed and extracted with I.B.M.K.

In a competing reaction system of the type shown, there would exist the complexonates having stability constants K_1, K_2, K_3, K_4 respectively, X being the complexone.

$$\mathrm{Mg} + \mathrm{S.A.B.F.} \overset{K_1}{\rightleftharpoons} \mathrm{Mg/S.A.B.F.}$$

$$\mathrm{Ni} + \mathrm{S.A.B.F.} \overset{K_2}{\rightleftharpoons} \mathrm{Ni/S.A.B.F.}$$

$$\mathrm{Mg} + \mathrm{X} \overset{K_3}{\rightleftharpoons} \mathrm{Mg/\ X}$$

$$\mathrm{Ni} + \mathrm{X} \overset{K_4}{\rightleftharpoons} \mathrm{Ni/\ X}$$

For the technique to be successful the following conditions must apply:-

(a) The Mg/S.A.B.F. complexonate must be more stable than the Ni/S.A.B.F. complexonate, i.e. $K_1 > K_2$

(b) $K_1 > K_3$

(c) $K_4 > K_3$

(d) $K_4 > K_2$

In order to design a system fulfilling these requirements, we studied the stability constants of a number of magnesium and nickel complexonates(7). This showed that the required conditions could not be achieved with the complexones listed, the exception being cyanide.

No data was available for the stability of S.A.B.F. complexonates but by the use of competing reactions, we were able to establish that for

Mg/S.A.B.F. $\log K < 1.36$

Ni/S.A.B.F. $\log K > 9.9 \quad < 11.70$

This was based on the fact that the fluorescence of the Mg/S.A.B.F. complex in solution was destroyed by the addition of a solution of citrate, tartrate, oxalate and complexones such as the disodium salt of ethelenediamine tetracetic acid (E.D.T.A.-Na_2). It was observed that in low concentrations, cyanide had no effect.

An extractable Ni/S.A.B.F. complex was formed in the presence of citrate, tartrate and oxalate but not in the presence of cyanide.

	log K	
Complexone	Magnesium	Nickel
Cyanide	Not quoted	11.70-31
Tartrate	1.36-7.9	6.9-9.9
Citrate	1.60-3.24	3.19-5.10
Oxalate	2.28	5.16-5.3
EDTA (Na_2)	8.69-9.72	17.4-18.56

3.4.2.1. Solvent Extraction of the Mg/.S.A.B.F. Complex from a Solution of Nickel Complexed by Cyanide.

Experiment had shown that a 6 x 10^3 molar excess of cyanide, had no effect on the fluorimetric determination of magnesium as the Mg/S.A.B.F. complex (Section 2.2.6). From this and the foregoing considerations, it was thought possible to determine magnesium in the presence of the large excess of cyanide necessary to keep 1g. nickel complexed in the aqueous phase.

Sample solutions containing 1 g. of 99.999% pure nickel were prepared by dissolving the metal in redistilled hydrochloric acid, evaporating just to dryness to remove excess acid and the residue dissolved in distilled water. To this solution was added 25 ml. 30% KCN to complex the nickel, giving a 10^6 molar excess of cyanide over the magnesium to be added.

In order to remove uncomplexed impurities from the sample solution, it was extracted as follows. 3 ml. of (2:1) pyridine/diethylamine were added, the pH adjusted to 12.3 with diethylamine, 2 ml. 0.02% S.A.B.F. added to develop the Mg/S.A.B.F. complex, which was subsequently extracted from the aqueous phase with two 10 ml. portions of I.B.M.K.

It was found necessary to repeat the extraction several times before the extract was colourless. After the sample solutions had stood for about 30 minutes and extracted as above, a coloured extract was again obtained.

obtained./.....

This suggested that even when impurities had been removed from the sample solution by extraction with S.A.B.F., after standing a few minutes, sufficient Ni^{2+} ions would be present as a result of the slow decomposition of the $[Ni(CN)_4]^{2-}$ complex to cause interference with the magnesium determination.

When purified, sample solutions were spiked with up to 5 µg Mg and the magnesium determined. Recoveries of only 29.5% were obtained with a single extraction. The extraction had to be repeated several times before all the magnesium was recovered from the aqueous phase.

The use of cyanide to complex the nickel was therefore considered unsuitable as it caused low recoveries of magnesium and did not complex the nickel sufficiently to prevent it interfering with the method.

We therefore concluded that the nickel had to be removed completely from solution before the Mg/S.A.B.F. complex was developed.

A study of solvent extraction systems (Ref.8) suggested several methods and the use of thiocyanate or thiocyanate/pyridine appeared to be the basis of a method which we could apply to the removal of a number of elements, e.g. tungsten, molybdenum, niobium and rhenium.

3.4.2.2. Solvent Extraction of Nickel as a Pyridine/thiocyanate Complex

When pyridine was added to a solution of a nickel salt, a deep blue coloured solution was produced, the addition of a solution of thiocyanate caused a pale blue precipitate to form. The precipitate was soluble in chloroform, leaving a colourless aqueous phase.

An experiment was performed to determine the molecular proportions of the reactants in the complex. This showed that nickel, pyridine and thiocyanate occurred in the molecular proportions of 1:4:2 respectively. No attempt was made to establish the structure of the complex.

EXPERIMENTAL

PART (A) 0.5 gm. of nickel as the sulphate in 40 mls. of distilled water was added to a 250 ml. separating funnel. 4 gm. of potassium thiocyanate in 10 ml. of distilled water was added so that thiocyanate could be present in excess. 40 ml. of chloroform was added and the mixture 'titrated' with pyridine until, with the addition of 0.1 ml. of pyridine, on extracting the complex with chloroform a completely colourless aqueous phase was obtained.

2.25 ml. of pyridine was required.

PART (B) 0.5 gm. of nickel as sulphate in 40 ml. of distilled water was added to a 250 ml. separating funnel and 10 ml. of pyridine added so that the pyridine was present in excess. 40 ml. of chloroform was added and the mixture 'titrated' with 10% aqueous potassium thiocyanate as above. 15.5 ml. of 10% potassium thiocyanate solution was required.

RESULTS

From Part A, 1.0 gm. of nickel required (0.982 x 2.75 x 2) = 5.40 gm. of pyridine

From Part B, 1.0 gm. of nickel required (1.55 x 2) = 3.10 gm. of potassium thiocyanate.

RESULTS (Continued)

Thus	Nickel	:	Pyridine	:	Potassium thiocyanate
Wt (g.)	1.0	:	5.40	:	3.10
Ratio of number of moles	$\frac{1}{58.71}$	:	$\frac{5.40}{74.10}$	:	$\frac{3.10}{65.70}$
	0.017	:	0.073	:	0.032
	1	:	4 approx	:	2 approx

The complex therefore has the composition (Ni), $(Py)_4(SCN)_2$.

The extraction procedure showed great promise . The nickel complex, being insoluble in water, when extracted with chloroform, completely removed one gramme of nickel from the aqueous phase in one step.

3.4.2.3. Calibration for the Fluorimetric Determination of Magnesium Using S.A.B.F. Following the Nickel. Extraction Procedure.

It was decided to perform a trial calibration using the nickel extraction procedure in the absence of nickel. This was to be followed by development of the Mg/S.A.B.F. complex in the aqueous phase and extraction with I.B.M.K.

The object of this experiment was to establish whether pyridine and thiocyanate added during the nickel extraction stage interfered with the subsequent determination of the magnesium.

We established that no interference occurred. Fig.1, a linear calibration graph being produced, of slope equal to that of the curve resulting from the normal procedure (Fig. 1).

EXPERIMENTAL

(1) To each of six 100 ml. separating funnels was added
40 ml. distilled water,
1, 2 etc-5.0 µg magnesium respectively,
15 ml. of nickel complexing solution (35 g. A.R. potassium thiocyanate and 60 ml. pyridine made to 100 ml. with distilled water).
50 ml. of chloroform,
Shake for about one minute, allow to stand until the chlorform surface is free of any pale blue nickel complex, leaving a colourless aqueous phase.

(2) Run off the lower dark blue chlorform phase.

(3) Extract the aqueous phase with 10 ml. of chloroform, followed by 10 ml. of I.B.M.K.
Run the lower nickel-free aqueous phase into a 250 ml. beaker.

(4) Add 1 ml. 1% KCN,
3 ml. pyridine/diethylamine (2:1) buffer.

(5) Adjust the pH to 12.3 with diethylamine.

(6) Add 2 ml. 0.02% S.A.B.F. in dioxan.

(7) Extract the complex with two 10 ml. portions of I.B.M.K. adding the extracts to 25 ml. graduated flasks.
Make to volume with I.B.M.K., dry with anhydrous sodium sulphate

(8) Read the fluorescence intensity.

Observations

A linear calibration graph was obtained over the range tested 0.0 - 5.0 µg Mg/25 ml. I.B.M.K. This was superimposed on the normal procedure curve (Fig.11).

The calibration factor was 0.241 µg Mg per 25 ml. I.B.M.K./galvanometer division. This showed that the extraction procedure for the removal of nickel did not interfere with the fluorimetric determination of the magnesium.

A second calibration was performed by this method, the sample solutions being spiked with a solution containing 1 gm. of nickel. This gave the calibration shown by Fig. 7. This was linear in the region 0.0 - 2.0 µg Mg having the same slope as Fig 1. Above 2.0 µg Mg, however, the slope decreased.

No explanation could be found for the change in slope of the graph at the 2 µg magnesium point.

The experiments were repeated using chloroform instead of I.B.M.K. to extract the Mg/S.A.B.F. complex. In the absence of nickel the sensitivity was increased, (Fig.8)

After the extraction of 1 gm. of nickel, the calibration was linear but of reduced sensitivity in 0 - 2.0 µg Mg range. Above this the slope decreased becoming negative at 3.3 µg Mg/25 ml. $CHCl_3$ (Fig.8)

From the foregoing it is apparent that the method is applicable in the range 0.0 - 2.0 µg Mg/25 ml. of I.B.M.K. or $CHCl_3$.

In order to extend the range of the method, we looked for a reason for the change in slope of the calibration graph above 2 µg Mg after 1 gm. of nickel had been extracted. The most likely explanation seemed to be the excess acid added when the sample solutions were "spiked" with a solution containing 1 g. of nickel. Measurement of the pH of the aqueous solutions at various stages throughout the method, in both the presence and the absence of nickel, showed this to be so. In the case of the former, it was necessary to add large volumes of diethylamine to obtain a pH of 12.3 (up to 5 ml. was necessary in some cases). As shown in Fig.5, this reduces the fluorescence intensity of the Mg/S.A.B.F. complex. Attempts were made to overcome this by a preliminary adjustment of the pH of the sample solution to a value of about 3.0, using sodium hydroxide solution, (at higher values nickel precipitated). This was followed by the procedure described, but it was not successful, giving scattered results.

A final attempt was made to overcome the problem of the change in slope of the calibration graph using the method described in Section 2.2.2., using 10% NaOH or HCl instead of diethylamine, to adjust the pH to 12.3. This gave a linear calibration in the range 0.0 - 2.0 µg Mg/25 ml. I.B.M.K. superimposable on Fig 1, changing in slope above this range.

Since no satisfactory explanation for the effect was found, it was decided to limit the method to the determination of 0.0 - 2.0 µg Mg.

The proposed method for the separation of one gramme quantities of nickel from 0.0 - 2.0 µg quantities of magnesium by solvent extraction and subsequent fluorimetric determination of the magnesium using the S.A.B.F. reagent is as follows:-

3.4.3. Method for the Fluorimetric Determination of Trace Amounts of Magnesium in Macro Amounts of Nickel by means of N.N'-Bis-Salicylidene-2,3-Diamino-Benzofuran (S.A.B.F.)

SUMMARY

The nickel sample for analysis is brought into aqueous solution with hydrochloric acid and evaporated to dryness to remove excess acid. The residue is then dissolved in distilled water and the nickel removed by solvent extraction with chloroform as the nickel/pyridine/thiocyanate complex.

After buffering the aqueous phase containing the magnesium, with a pyridine/diethylamine solution, to a pH of 12.3, the magnesium/S.A.B.F. complex is extracted with iso-butyl methyl ketone and the fluorescence intensity of the extract measured.

Precision at 95% confidence level is ± 0.05 µg Mg/25 ml. I.B.M.K.

When estimating 1.0 µg Mg.

(1)	Magnesium standard :- (100 µg Mg/ml. (STOCK SOLUTION)	Dissolve 0.08[illegible]1 g of magnesium oxide (Johnson Matthey "Spec Pure") in 5 ml. of redistilled 6M hydrochloric acid dilute to 500 ml.
(2)	Magnesium standard :- (1 µg Mg/ml.) (WORKING SOLUTION)	Dilute 1 ml. of stock solution to 100 ml. with distilled water
(3)	Pyridine/thiocyanate:- solution	Dissolve 175 g. A.R. potassium thiocyanate in 125 ml. of distilled water, add 300 ml. of A.R. pyridine, dilute to 500 ml. with distilled water.
(4)	1% (w/v) potassium :- cyanide	Dissolve 1 g. of potassium cyanide in distilled water and dilute to 100 ml.
(5)	Pyridine/diethylamine:- (2:1) (Buffer solution)	Add 60 ml. of A.R. pyridine to 30 ml. of A.R. diethylamine.
(6)	A.R. chloroform.	
(7)	A.R. iso-butylmethyl ketone (I.B.M.K.)	
(8)	A.R. sodium sulphate (anhydrous)	
(9)	A.R. hydrochloric acid.	

Preparation of Sample

(1) Accurately weigh about 1 g. of nickel sample and add to a 250 ml. beaker containing about 50 ml. of distilled water.

(2) Add 40 ml. of redistilled 6M hydrochloric acid, cover the beaker with a watch-glass.

(3) Allow the first vigorous reaction to subside, then gently heat on a hot plate until all the sample has dissolved.

Preparation of Sample (Continued)

(4) Evaporate almost to dryness, cool, transfer to a waterbath and heat to dryness.

(5) Dissolve the residue in 40 ml. of distilled water, warming on the waterbath unitl all the residue has dissolved. Cool the solution.

Extraction of the Nickel from the Magnesium

(6) Transfer the prepared sample solution to a 100 ml. separating funnel containing 50 ml. A.R, chloroform.

Add 15 ml. of pyridine/thiocyanate solution.

Shake until all the nickel complex has dissolved in the chloroform, leaving a clear aqueous layer.

(7) Run off the lower deep blue chloroform layer and reject.

(8) Wash the aqueous layer by extracting with 10 ml. of chloroform, reject, wash with 10 ml. of I.B.M.K.

Allow the phases to separate.

(9) Run the lower aqueous phase into a 150 ml.beaker together with aqueous washings from the separating funnel.

Development of the Mg/S.A.B.F. Complex and Fluorimetric Measurement.

(10) To the aqueous layer add,
1 ml. 1% potassium cyanide
3 ml. pyridine/diethylamine buffer (2:1)

(11) Adjust the pH of the solution to 12.3 with diethylamine.

(12) Add 2 ml. 0.02% S.A.B.F. reagent

(13) Transfer the solution to 250 ml. separating funnels. Extract twice with 10 ml. portions of I.B.M.K. Add the extract to 25 ml. graduated flasks and make to volume with I.B.M.K.

(14) Dry the extract with a little finely powdered anhydrous sodium sulphate.

(15) Read the fluorescence of the extract in a 1 cm. path length rectangular sample cell, using incident excitation light of wavelength 493 n.m.

(15) .. 493 n.m./...

and measuring the fluorescent light at a wavelength of 620 n.m.

(16) From a calibration graph determine the concentration of magnesium in the sample.

CALIBRATION

(1) To each of five 250 ml. beakers add
40 ml. of distilled water
0.5, 1.0, 1.5. 2.0 µg magnesium

(2) Transfer the solution to a 100 ml. separating fu... l.

(3) Proceed as for method stages (6) to (16)

Prepare a calibration graph of fluorescence intensity versus magnesium concentration.

4. CONCLUSIONS AND FUTURE WORK

The research discussed in this report has been devoted to two main problems.

(1) The preparation, investigation and development of the new fluorimetric reagent for magnesium, N.N'-bis-salicylidene-2,3-diaminobenzofuran (S.A.B.F.)

(2) Investigation of methods for the separation of traces of magnesium frm gram quantities of various matrix elements, and the subsequent determination of the trace constituent.

The first section has proved to be completely successful, the reagent is easy to prepare, simple to use and provides a very sensitive means of determining magnesium at sub-microgram levels. It is the most sensitive fluorimetric reagent for magnesium so far tested.

The second and much larger problem has been partially solved, in that a method has been developed for the separation and determination of microgram quantities of magnesium from 1 gram of nickel. The procedure, involving the preliminary solvent extraction of the nickel, followed by fluorimetric determination of the magnesium as the S.A.B.F. complex, is straightforward and fairly rapid.

Repeat determinations of synthetic standards containing 1 µg Mg have indicated a precision of ± 0.05 µg Mg/25 ml. solvent at the 95% confidence level.

The same separation procedure should be applicable to the separation of traces of aluminium from nickel, followed by estimation of the aluminium using the reagent A.H.F.S. tested in our 1965-66 programme(10).

This procedure will not, however, be applicable to any of the other separations required by the terms of this contract.

In view of the lack of success obtained using other separation techniques such as ion-exchange chromatography, it is clear that a new approach is required.

It is proposed, therefore, that the method of carrier precipitation of the trace constituents should be investigated. In this procedure the matrix material is held in solution as a soluble complex while the required trace element is precipitated by a suitable reagent, together with a quantity of an added carrier element, which ensures the complete removal of the required element. The determination of the required element may then be carried out after masking, or removing, the carrier element. Considerable care is needed in the choice of the nature and quantity of carrier element to be used, and in the type of precipitation reaction employed.

In the first instance, it is proposed that the separation of magnesium from titanium by this technique should be examined. Titanium will be held in solution as the peroxy complex $[TiO_2(SO_4)_2]^{2-}$ and a few hundred micrograms of iron or nickel will be used as a carrier, this will subsequently be masked with cyanide for the final estimation of magnesium with the reagent S.A.B.F. If this is successful, it should be possible to apply a similar technique to the determination of aluminium in titanium and both magnesium and aluminium in molybdenum, niobium and tungsten.

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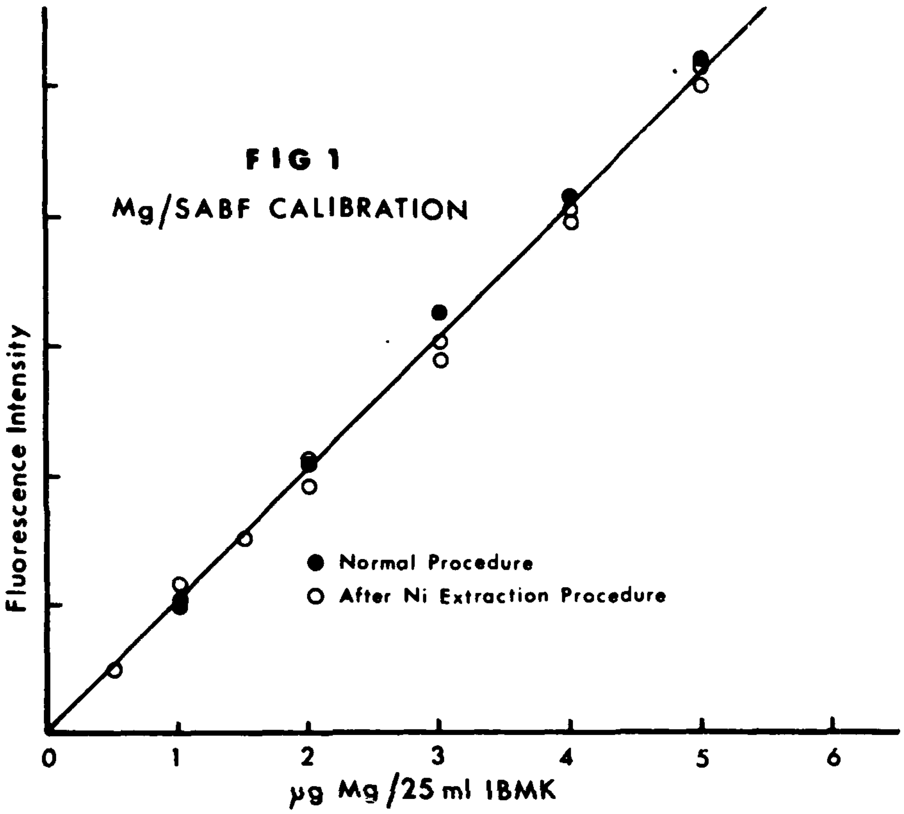


FIG 1

Mg/SABF CALIBRATION

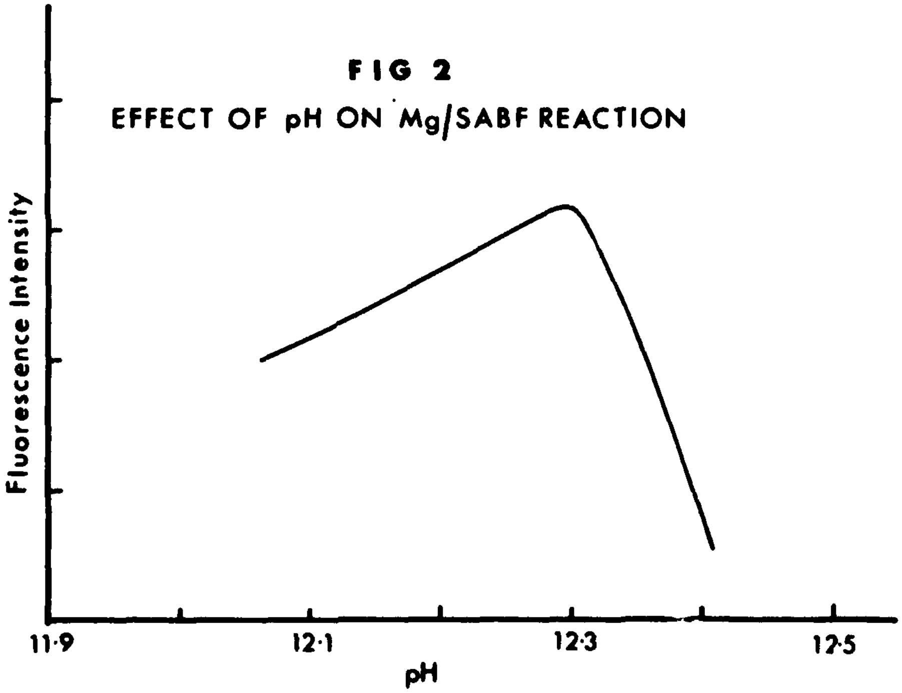


FIG 2

EFFECT OF pH ON Mg/SABF REACTION

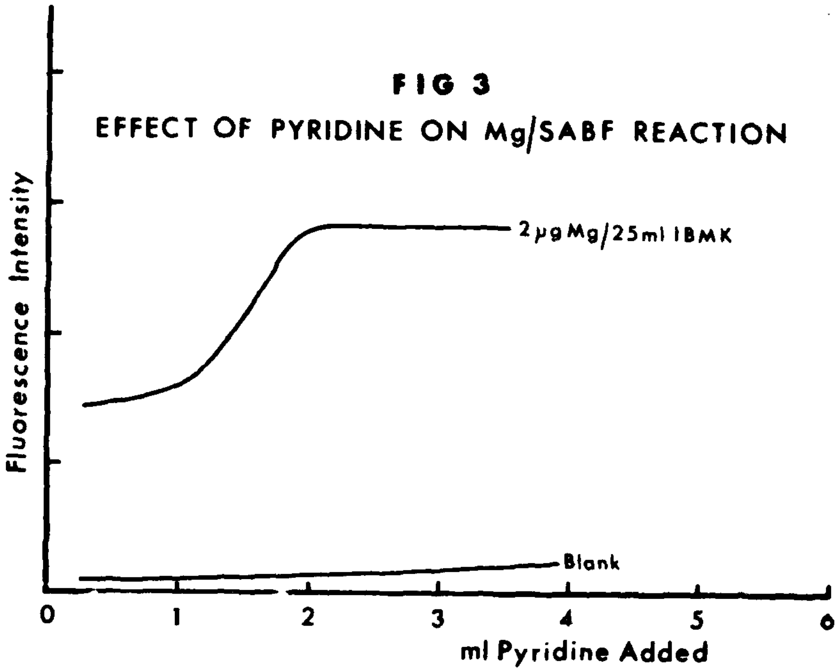


FIG 3

EFFECT OF PYRIDINE ON Mg/SABF REACTION

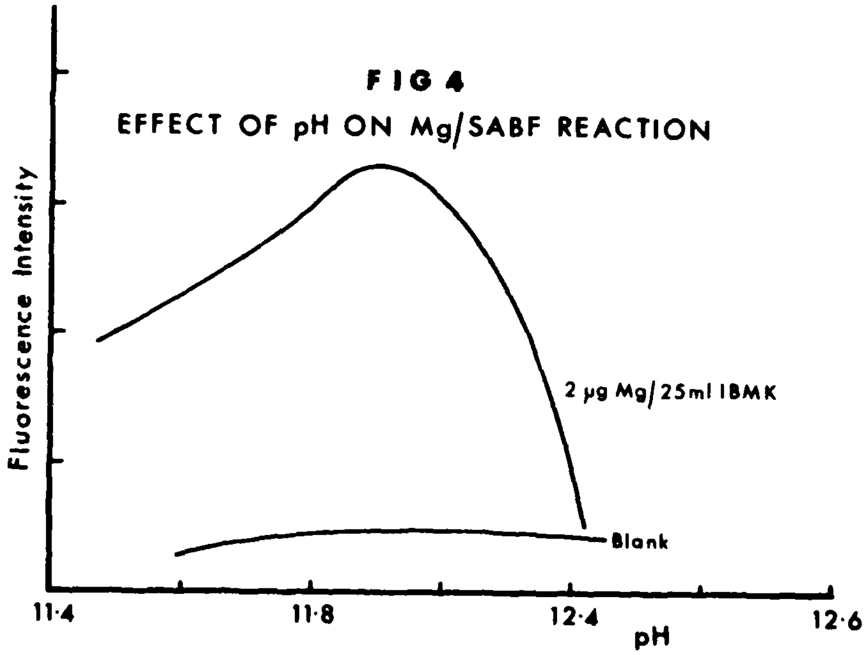


FIG 4

EFFECT OF pH ON Mg/SABF REACTION

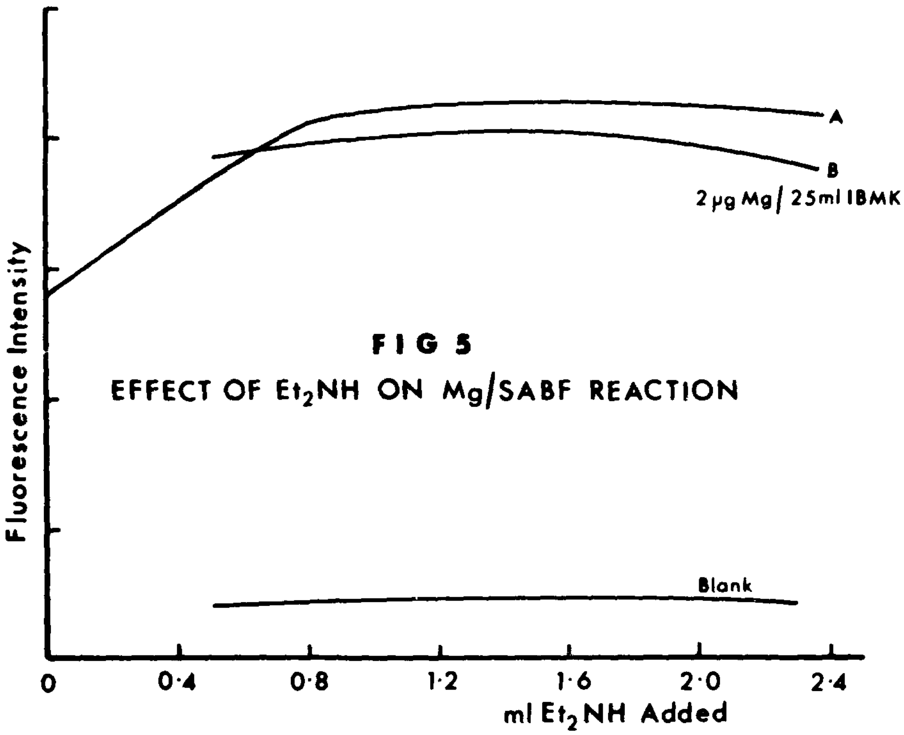


FIG 5

EFFECT OF Et_2NH ON Mg/SABF REACTION

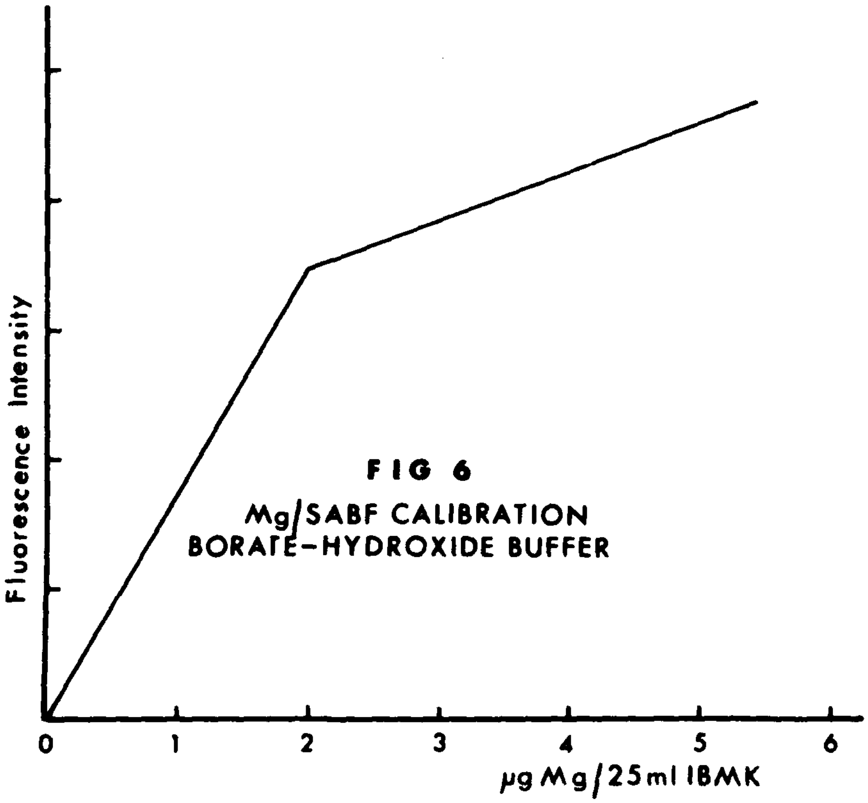


FIG 6

Mg/SABF CALIBRATION
BORATE–HYDROXIDE BUFFER

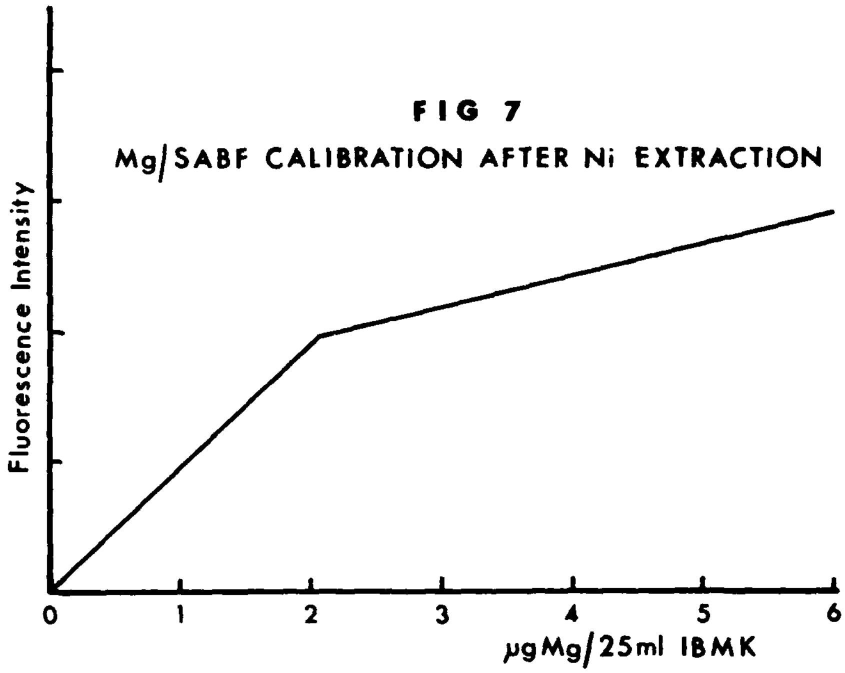


FIG 7

Mg/SABF CALIBRATION AFTER Ni EXTRACTION

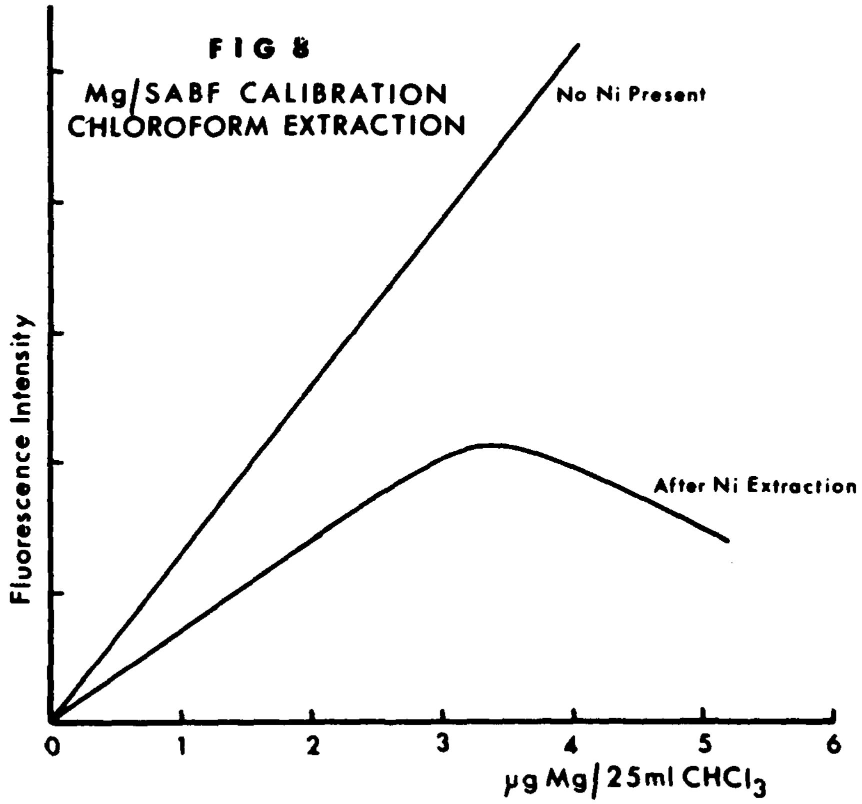


FIG 8

Mg/SABF CALIBRATION
CHLOROFORM EXTRACTION

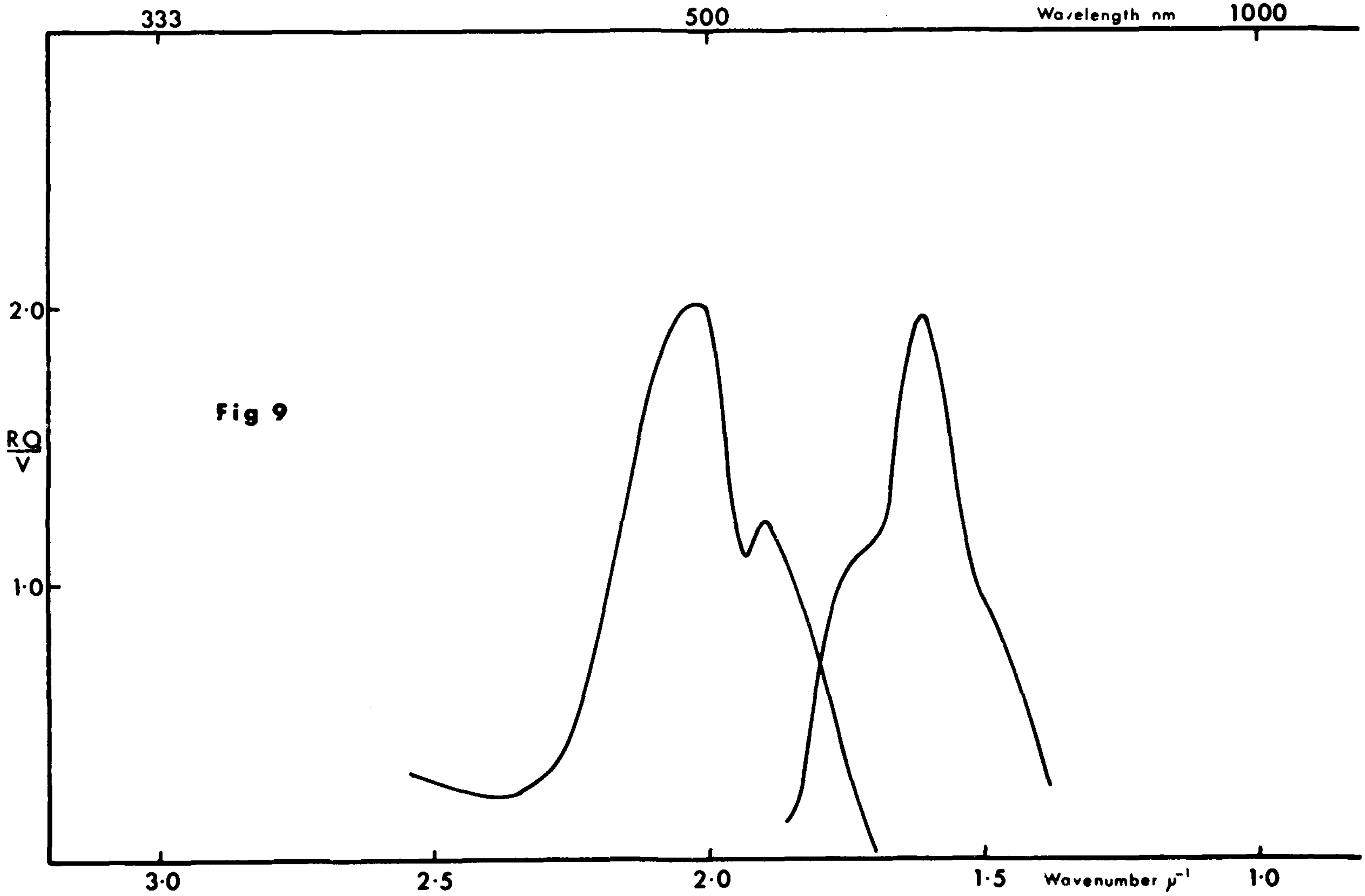
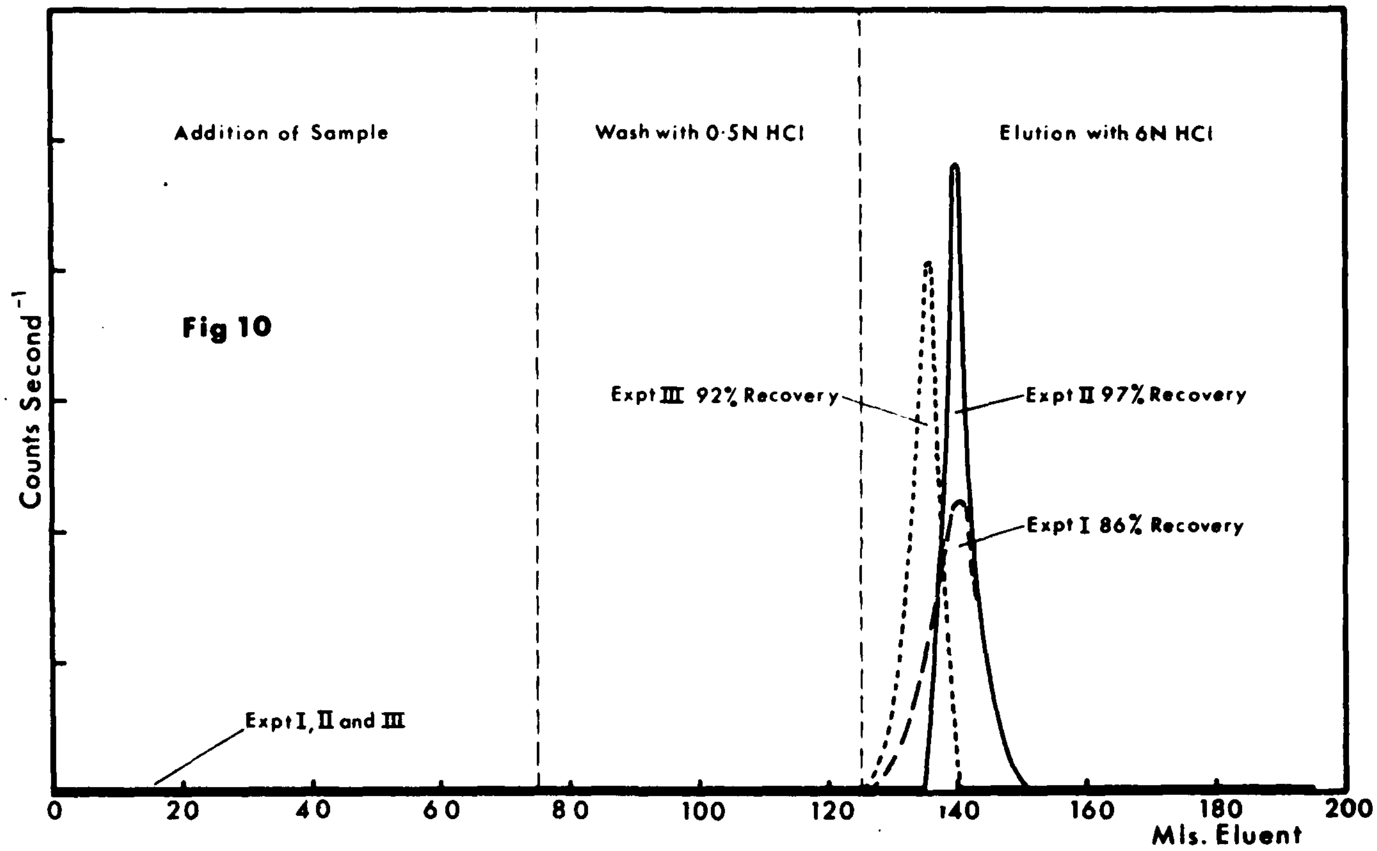


Fig 9

Mg – N,N′-BIS(SALICYLIDENE)-2,3-DIAMINOBENZOFURAN

Fig 10



BEHAVIOUR OF Mg^{28} ON CATIONIC-EXCHANGE COLUMN

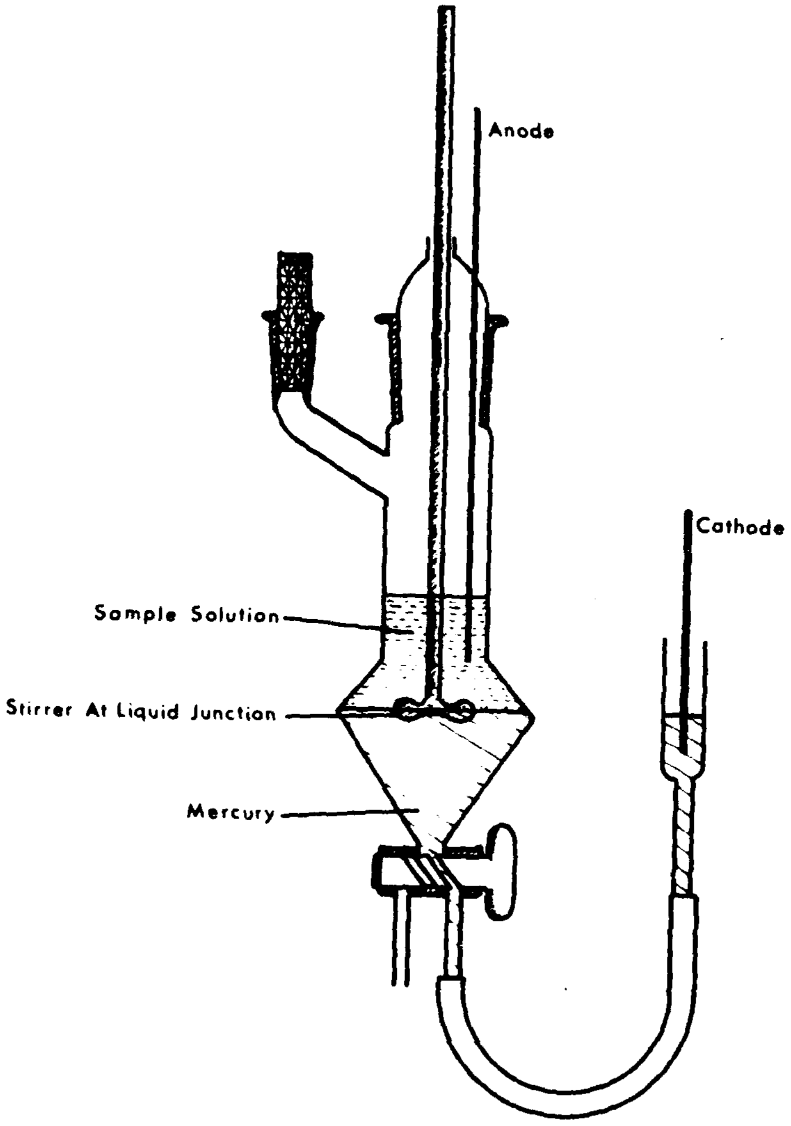


FIG 11
MODIFIED MELAVEN CELL

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3 REPORT TITLE

Study of the Estimation of Certain Trace Impurities by Fluorimetric Methods

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Technical Report: September 1966 - August 1967

5 AUTHOR(S) *(Last name, first name, initial)*

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6 REPORT DATE November 1967	7a TOTAL NO OF PAGES 40	7b NO OF REFS 10

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY US Army Research and Development Group (Europe) APO New York 09757

13 ABSTRACT

Work carried out during the fourth year of the present contract is reported.

The preparation and development of a new fluorimetric reagent for magnesium is described. This is N,N'-bis salicylidene-2,3-diaminobenzofuran. The spectral characteristics of the magnesium complex are given together with evidence to show that this is the most sensitive magnesium reagent so far tested in this program.

Details are given of work on the development of separation techniques for the removal of microgram quantities of magnesium from gram quantities of molybdenum and nickel. Full experimental data is presented concerning a new method for the determination of up to 2 p.p.m. magnesium in nickel.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Analytical Chemistry						
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