THE DETERMINATION OF SELECTED LANTHANOID ELEMENTS BY ATOMIC-ABSORPTION SPECTROSCOPY USING ELECTROTHERMAL ATOMIZATION

by

J. Haines

20th December, 1985

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SYNOPSIS

Optimum ashing and atomization temperatures were established for the following lanthanoids in synthetic solutions containing 1 per cent hydrochloric or nitric acid: praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

Samarium, europium, and terbium were subsequently investigated in more detail. Atomization from a tantalum surface greatly improved the efficiency of atomization of terbium but hardly affected that of samarium and europium. Tantalum-metal strips, boats, and platforms were found to be superior to tantalum carbide coatings for this purpose. Interference effects from the other lanthanoids and yttrium on the response of the analyte were established across the widest possible analytical range at ratios of interferent to analyte of 10, 50, and 100:1 and were found to be most severe for terbium and least severe for europium.

Several reference materials were analysed for ten of the lanthanoids, and it was found that samarium, europium, thulium, and ytterbium can be determined direct by atomic-absorption spectroscopy using electrothermal atomization; holmium, erbium, and dysprosium require the use of the method of analyte additions; and terbium, lutetium, and gadolinium cannot be measured by this method with any degree of accuracy.

The laboratory method for the determination of samarium, europium, thulium, and ytterbium is detailed in an appendix.

SAMEVATTING

Optimale verassings- en verstuiwingstemperature is vir die volgende lantanoiede in sintetiese oplossings wat 1 persent sout- of salpetersuur bevat, vasgestel: praseodimium, neodimium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium en lutetium.

Samarium, europium en terbium is vervolgens in meer besonderhede ondersoek. Verstuiwing vanaf 'n tantaaloppervlak het die doeltreffendheid van terbiumverstuiwing baie verbeter, maar feitlik geen uitwerking op die verstuiwing van samarium en europium gehad nie. Daar is gevind dat tantaalmetaalstrokke, -skuitjies en -platforms beter as tantaalkarbiedbedekkings is vir hierdie doel. Die steuringseffekte van die ander lantanoiede en yttrium op die reaksie van die analiet is oor die grootste moontlike analitiese bestek met verhoudings van 10, 50 en 100:1 vir die interferent tot die analiet bepaal, en daar is gevind dat dit die ernstigste vir terbium en die geringste vir europium is.

Verskeie verwysingsmateriale is vir tien van die lantanoiede ontleed en daar is gevind dat samarium, europium, thulium en ytterbium regstreeks deur atoomabsorpsiespektroskopie met gebruik van elektrotermiese verstuiwing bepaal kan word; holmium, erbium en dysprosium vereis die gebruik van die metode van analietbyvoegings; en terbium, lutetium en gadolinium kan nie met enige mate van akkuraatheid volgens hierdie metode gemeet word nie.

Die laboratoriummetode vir die bepaling van samarium, europium, thulium en ytterbium word in besonderhede in 'n aanhangsel uiteengesit.
1. INTRODUCTION

The lanthanoid elements are gaining in importance in many fields of application. One of the major applications is the addition of these elements to various steels to increase their resistance to oxidation or their malleability. Gadolinium, samarium, europium, and dysprosium are used in the nuclear industry, and the lanthanoids are of importance in the glass industry as polishing compounds and as colouring agents. Other applications of the lanthanoids include their use in carbon-arc lighting, television tubes, garnets, and hydrocarbon catalysts, and in the manufacture of very small magnets for the semiconductor industry.

Several analytical techniques are available for the measurement of the lanthanoid elements. These include atomic emission spectrometry (AES) using inductively coupled plasma (ICP), X-ray-fluorescence spectrometry (XRFS), mass spectrometry (MS), ion chromatography (IC), and atomic-absorption spectroscopy (AAS) using flame atomization or electrothermal atomization (ETA).

AAS has been used as an analytical tool for nearly thirty years. The introduction of ETA improved the detection limits for most elements by up to three orders of magnitude, and this increased sensitivity should allow the lanthanoids to be measured at lower concentrations than those normally achieved when other techniques are used.

ETA has been used in the measurement of individual or selected groups of the lanthanoids. Fuavao and Sneddon measured ytterbium and compared its atomization from a furnace wall, a platform, and a microboat. Grobenski measured all the lanthanoids by ETA-AAS, using pyrolytically coated and uncoated graphite furnaces, and postulated a possible atomization mechanism. Sen Gupta determined the lanthanoids and yttrium in rocks and in sixteen international reference materials of rock and coal. Horsky and Fletcher used a procedure combining ion exchange and ETA-AAS to determine five of the lanthanoids in geological samples. L'vov and Pelieva lined a graphite furnace with tantalum foil, and found that the sensitivity improved for all the lanthanoids tested. Mazzucotelli et al. investigated the determination of dysprosium, europium, thulium, holmium, and ytterbium by ETA-AAS using a graphite furnace, and interference effects in the determination of ytterbium, holmium, dysprosium, thulium, and europium.

The present investigation was undertaken so that the applicability of ETA in the determination of the lanthanoids could be established. This would include optimization of the furnace parameters, the investigation of interference effects and of methods by which they can be overcome, and the development of an analytical method for the determination of as many of the lanthanoids as possible.

2. EXPERIMENTAL METHODS

2.1. Apparatus and Reagents

A Varian AA1475 atomic-absorption spectrophotometer was used in conjunction with a Varian GTA-95 graphite-furnace atomizer. The system is equipped with an autosampler for the injection of predetermined volumes of sample into the graphite furnace.

Unless otherwise stated, pyrolytically coated tubes were used.

Separate standard stock solutions of praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium, and lutetium were prepared by dissolution of their oxides (Spec-pure grade) in hydrochloric or nitric acid. Solutions were diluted for use with 1 per cent (v/v) A.R.-grade hydrochloric or nitric acid. All the other solutions were of A.R. grade.

2.2. Instrumental Conditions

The resonance wavelengths and lamp currents used are detailed in Table 1. A spectral bandwidth of 0.2 nm was used for the determination of all the lanthanoids in an effort to reduce the possibility of incandescence. The alignment of the graphite furnace in the light path was optimized for the same reason.

2.3. Optimization of Conditions for Measurement

The operating conditions were examined for twelve of the lanthanoids (viz. dysprosium, erbium, europium, gadolinium, holmium, neodymium, praseodymium, samarium, terbium, thulium, ytterbium, and lutetium) in two sets of synthetic standard solutions, one of which contained 1 per cent (v/v) hydrochloric acid and the other 1 per cent (v/v) nitric acid.
DETERMINATION OF LANTHANOID ELEMENTS

TABLE 1

Wavelengths and lamp currents used in the measurement of the lanthanoids

<table>
<thead>
<tr>
<th>Lanthanoid</th>
<th>Lamp current mA</th>
<th>Wavelength nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Praseodymium</td>
<td>15</td>
<td>495.14</td>
</tr>
<tr>
<td>Neodymium</td>
<td>15</td>
<td>463.42</td>
</tr>
<tr>
<td>Samarium</td>
<td>8</td>
<td>429.67</td>
</tr>
<tr>
<td>Europium</td>
<td>8</td>
<td>459.40</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>10</td>
<td>407.87</td>
</tr>
<tr>
<td>Terbium</td>
<td>10</td>
<td>432.65</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>10</td>
<td>421.17</td>
</tr>
<tr>
<td>Holmium</td>
<td>10</td>
<td>410.38</td>
</tr>
<tr>
<td>Erbium</td>
<td>10</td>
<td>401.80</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>10</td>
<td>371.79</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>15</td>
<td>398.80</td>
</tr>
<tr>
<td>Lutetium</td>
<td>10</td>
<td>335.96</td>
</tr>
</tbody>
</table>

2.3.1. Drying Stage

A dentist's mirror was used so that the sample could be observed drying in the furnace. It was found that a temperature of 95 °C allowed uniform drying with no sputtering, and that the drying time was dependent on the volume of solution injected into the furnace, a time of 55 seconds being required for 25 µl of sample to dry.

2.3.2. Ashing Stage

The ashing temperature was determined as follows: the atomization temperature was set to 2800 °C and the drying temperature to the optimum, and the ashing temperature was varied while the atomization peak height was recorded. A decrease in the atomization peak height is usually an indication of loss of analyte due to volatilization. For the lanthanoids, an increase in the ashing temperature at temperatures well below the volatilization temperature of these elements resulted in a decrease in peak height, which was not due to loss of the analyte, but probably occurred as a result of the formation of refractory compounds. This phenomenon is usually associated with carbide-forming elements, since there is a greater probability of carbide formation at elevated temperatures. Therefore, in most instances, the ashing temperature chosen as the optimum was not necessarily the temperature at which maximum sensitivity was obtained but that at which the loss in sensitivity was not due to volatilization of the analyte. The ashing time for the simple hydrochloric acid or nitric acid matrix was 10 seconds. The ashing temperatures used for the measurement of the twelve elements in a synthetic acid solution are shown in Table 2.

TABLE 2

Conditions for the measurement of the lanthanoids in synthetic solutions

<table>
<thead>
<tr>
<th>Lanthanoid</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ashing</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>700</td>
</tr>
<tr>
<td>Neodymium</td>
<td>900</td>
</tr>
<tr>
<td>Samarium</td>
<td>800</td>
</tr>
<tr>
<td>Europium</td>
<td>700</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>900</td>
</tr>
<tr>
<td>Terbium</td>
<td>600</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>700</td>
</tr>
<tr>
<td>Holmium</td>
<td>700</td>
</tr>
<tr>
<td>Erbium</td>
<td>800</td>
</tr>
<tr>
<td>Thulium</td>
<td>700</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>900</td>
</tr>
<tr>
<td>Lutetium</td>
<td>800</td>
</tr>
</tbody>
</table>
2.3.3. Atomization Stage

The optimum temperature for atomization was determined while the drying and ashing temperatures were maintained at the optimum level and the atomization temperature was varied. As would be expected, it was found that an increase in atomization temperature caused an increase in peak height. However, the lanthanoids are known to form refractory compounds in the furnace, and the effect of increased atomization temperature on the peak height of the blank solution (i.e. atomization of the acid alone after atomization of the analyte) was also tested. Photo-emission from the furnace walls at high temperatures severely affected the measurement of some of the lanthanoids (Figure 1); lower atomization temperatures resulted in incomplete volatilization of the analyte, giving rise to 'memory effects'. Therefore, the atomization temperature chosen as the optimum was that for which the sensitivity for the analyte was reasonable but the 'memory effect' was not severe.

The atomization temperatures used are detailed in Table 2.

The atomization temperature was maintained for only 5 seconds, since longer atomization times did not effectively reduce the peak height of the blank solution further, but only served to reduce the usable life of the graphite furnace.

In all instances, the same conditions were used for the synthetic solutions in hydrochloric acid as for those in nitric acid.

2.4. Sensitivity and Precision of Measurement

Calibration curves were plotted for each of the lanthanoids in 1 per cent (v/v) solutions of hydrochloric acid or nitric acid, and it was found that the results obtained for thulium, ytterbium, and europium in the two acids were comparable. However, the sensitivity for the other lanthanoids at higher analyte concentrations was better in hydrochloric acid than it was in nitric acid. This may be due to the formation of refractory compounds in the nitric acid matrix, which inhibits volatilization of the lanthanoid from the graphite surface.

From these results, the quantity of each lanthanoid required to give an atomization peak height of 0.100 absorbance units (minus the absorbance of the blank solution) was calculated. The values obtained for each of the lanthanoids were compared, and the relative sensitivities were calculated, plotted, and compared with the boiling points of the lanthanoid metals and their heats of sublimation (Figure 2). These results are comparable with those of Grobenski, and suggest that the change in electronic structure is the same for boiling as for sublimation and is linked directly to the number of free atoms present, i.e. the sensitivity.

An indication of the relative variation in optimum precision was obtained for each element in synthetic solution (Table 3). For most elements, the precision in nitric acid was slightly inferior to that in hydrochloric acid, which is probably because of the increased amount of oxygen in the system with the nitric acid matrix.

2.5. Atomization Profiles

The shape of the atomization peak for an element is indicative of the manner in which that element volatilizes from the surface of the graphite furnace. Ideally, a Gaussian peak should be obtained, but this is rarely the case. A double atomization peak can indicate two atomization processes, the atomization of two distinct mineral phases, or interference from the matrix. An atomization peak that rises to a maximum but falls slowly to the base line and tails off very gradually can be indicative of the formation of refractory compounds. The comparison of atomization peaks from different types of surfaces, e.g. a graphite surface to a metal surface, is also useful. For these reasons, the atomization profiles of terbium, samarium, and europium were investigated.

By use of a programme facility offered by the Varian GTA-95 graphite-furnace atomizer, a printed copy of the curves of absorbance versus time was obtained, and hence the atomization profiles.

Under the optimum conditions determined, curves of absorbance versus time were established for the atomization of samarium, europium, and terbium from a graphite surface. For purposes of comparison, these elements were also atomized from a tantalum surface.
FIGURE 1. Effect of atomization temperature on the peaks for the blank solutions and the lanthanoids.
FIGURE 2. Relative sensitivities, heats of sublimation, and boiling points for the lanthanoids
TABLE 3

Precision of measurement for the lanthanoids in synthetic solutions

<table>
<thead>
<tr>
<th>Lanthanoid</th>
<th>Acid medium (v/v)</th>
<th>s_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>Praseodymium</td>
<td>HCl</td>
<td>0.065</td>
</tr>
<tr>
<td>Neodymium</td>
<td>HCl</td>
<td>0.044</td>
</tr>
<tr>
<td>Neodymium</td>
<td>HNO_3</td>
<td>0.078</td>
</tr>
<tr>
<td>Samarium</td>
<td>HCl</td>
<td>0.024</td>
</tr>
<tr>
<td>Samarium</td>
<td>HNO_3</td>
<td>0.056</td>
</tr>
<tr>
<td>Europium</td>
<td>HCl</td>
<td>0.028</td>
</tr>
<tr>
<td>Europium</td>
<td>HNO_3</td>
<td>0.028</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>HCl</td>
<td>0.095</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>HNO_3</td>
<td>0.150</td>
</tr>
<tr>
<td>Terbium</td>
<td>HCl</td>
<td>0.045</td>
</tr>
<tr>
<td>Terbium</td>
<td>HNO_3</td>
<td>0.082</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>HCl</td>
<td>0.041</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>HNO_3</td>
<td>0.061</td>
</tr>
<tr>
<td>Holmium</td>
<td>HCl</td>
<td>0.021</td>
</tr>
<tr>
<td>Holmium</td>
<td>HNO_3</td>
<td>0.045</td>
</tr>
<tr>
<td>Erbium</td>
<td>HCl</td>
<td>0.020</td>
</tr>
<tr>
<td>Erbium</td>
<td>HNO_3</td>
<td>0.060</td>
</tr>
<tr>
<td>Thulium</td>
<td>HCl</td>
<td>0.031</td>
</tr>
<tr>
<td>Thulium</td>
<td>HNO_3</td>
<td>0.041</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>HCl</td>
<td>0.022</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>HNO_3</td>
<td>0.024</td>
</tr>
<tr>
<td>Lutetium</td>
<td>HCl</td>
<td>0.045</td>
</tr>
<tr>
<td>Lutetium</td>
<td>HNO_3</td>
<td>0.056</td>
</tr>
</tbody>
</table>

Tantalum inserts were made from pure tantalum foil of 0.062 mm thickness. These inserts were shaped to fit closely inside the graphite furnace, and the analyte was injected onto and atomized from this surface. The operating conditions had to be changed since the melting point of tantalum is 2996 °C. A maximum temperature of 2500 °C was used for atomization, since higher temperatures damaged the surface of the tantalum, causing it to become very brittle. The drying temperature was increased to facilitate more-uniform drying.

The two atomization profiles for each of the analytes are compared in Figure 3. The profiles for the atomization of samarium and europium from tantalum and graphite surfaces are comparable, suggesting similar atomization processes for the two surfaces. However, the profile for the atomization of terbium from a graphite surface has a peak that is not very sharp and tails off gradually at the end of the atomization cycle (a of Figure 3). The profile for the atomization of terbium from tantalum has a peak that rapidly returns to base line (b of Figure 3). This suggests that atomization from graphite and tantalum occurs by two different processes. When terbium is atomized from graphite, a highly refractory compound is formed that is not completely atomized. This compound may be a carbide, since it does not form during the atomization of terbium from tantalum.

The tantalum insert was found to be unpractical since the tantalum began to curl at the edges after only one atomization. This reduced the contact surface and resulted in arcing, and hence irregular heating of the tantalum. After only five atomizations, the tantalum became very brittle and could not be used. A longer piece of tantalum foil, this time 0.018 mm thick, was used, the foil being cut and shaped to fit inside the furnace and to extend out of each end of the furnace. Consequently, when the graphite furnace was placed in the furnace-assembly system, the tantalum was in contact with the graphite collars, which
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(a) Terbium: graphite surface  
(b) Terbium: tantalum surface

(c) Samarium: graphite surface  
(d) Samarium: tantalum surface

(e) Europium: graphite surface  
(f) Europium: tantalum surface

Temperature, °C  
Absorbance

Time

FIGURE 3. Atomization profiles of terbium, samarium, and europium from graphite and tantalum surfaces
DETERMINATION OF LANTHANOID ELEMENTS

facilitated more-regular heating of the tantalum. The results obtained with this type of tantalum surface were similar to those obtained with the first tantalum insert, but were more reproducible. However, the lifetime of the insert did not improve.

Experiments in which tantalum boats and tantalum platforms were used were also unsuccessful because of the temperature lag between the wall and the boat, or between the wall and the platform.

An attempt was then made to form a coating of tantalum carbide on an unpyrolytically coated graphite furnace. The method used was that of Fritzschel et al.\textsuperscript{10}, who soaked a graphite furnace overnight in a 5 per cent solution of tantalum in hydrofluoric acid, and dried it at 120 °C for 2 to 4 hours. Prior to atomization, they heated the furnace to 120 °C for 1 minute, to 400 °C for 30 seconds, and finally to 2200 °C within 90 seconds, and held it at maximum temperature for 10 seconds. This procedure was repeated twice. In the present work, tests using such a furnace were then carried out on terbium, but the atomization peak obtained was found to be less sensitive than that from a pyrolytically coated furnace. The atomization of terbium from an unpyrolytically coated graphite furnace resulted in a peak that was not dissimilar from the peak obtained from the carbide coated surface. The sensitivity was poor, and the atomization peak was broad, with gradual tailing. It was thought that soaking of the furnace in the tantalum solution under vacuum would improve the carbide coating, but this procedure did not produce better results. It was concluded that this type of carbide coating does not effect any improvement in atomization, possibly because there is some sort of chemical reaction between the terbium and the tantalum carbide, but it is more likely that the coating was not satisfactory.

2.6. Interference

A comprehensive investigation of interference effects for all twelve of the lanthanoids was not practicable, and it was expected that an investigation of three of the elements, carefully chosen for their differing atomization characteristics and sensitivity, would indicate interference patterns for the other lanthanoids. Europium was chosen because its measurement by ETA-AAS is relatively uncomplicated and because it is one of the more sensitive elements. Terbium was chosen because its measurement by ETA-AAS is fairly complicated, and its sensitivity is poor. Finally, samarium was chosen because its sensitivity and ease of measurement is somewhere between those of europium and terbium.

The effect of increasing quantities of hydrochloric and nitric acids on the analyte response was tested, as were the interelement interference from the other lanthanoids and from yttrium. In these tests, the ratio of interferent to analyte was varied between 10:1 and 100:1, and the interference was tested across the entire calibration range.

2.6.1. Effect of Increasing Concentrations of Acid

In a hydrochloric acid matrix, the chloride complex is usually present before atomization but, in a nitric acid matrix, the nitrates usually dissociate thermally to the oxides. However, the lanthanoid chlorides all hydrolyse to the oxychlorides on evaporation, and above 1000 °C these decompose to the oxide. Therefore, for the lanthanoids, the oxide intermediate can be expected to form before atomization in both acid media.

The optimum conditions for atomization established previously were used in the tests on the effect of increasing concentrations of hydrochloric and nitric acids on the analyte response, but the concentrations of hydrochloric acid and nitric acid were varied from 0.05 to 3.0 M and from 0.06 to 4.0 M respectively.

For europium, increasing quantities of hydrochloric or nitric acid did not affect the atomization peak height. This suggests that the atomization process is not influenced by large quantities of either oxygen or hydrogen chloride gas.

For samarium, increasing quantities of hydrochloric acid did not influence the height of the atomization peak. However, nitric acid in concentrations greater than 0.4 M suppressed the atomization peak and, at concentrations in excess of 2.0 M, resulted in a double atomization peak.

For terbium, the peak height decreased slightly as the concentration of hydrochloric acid was increased from 0.05 to 0.5 M, but remained constant at concentrations higher than that level. At nitric acid concentrations higher than 0.4 M, there was severe suppression of the atomization peak and at concentrations exceeding 1.0 M, a double atomization peak was exhibited.
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At high temperatures, nitric acid decomposes to oxygen and nitrogen oxides. These species may not affect the atomization process at low concentrations of nitric acid but, at high concentrations, the excess oxygen in the system may interfere with the process in some way. There are two possible reasons for this interference: the elemental species may recombine to form oxides in the vapour phase, or the excess oxygen present may inhibit dissociation of the oxide before atomization. It is to be expected that the sesquioxides would be converted to the monoxide before atomization. Although these oxides are not stable for most of the lanthanoids, they may be formed under certain conditions of temperature and pressure. Thermodynamic principles would predict that terbium forms the most stable monoxide (bond-dissociation energy 704 kJ/mol), followed by samarium (bond-dissociation energy 567 kJ/mol) and europium (bond-dissociation energy 479 kJ/mol). Therefore it seems likely that this effect would be most evident for terbium and least evident for europium.

2.6.2. Interelement Interference

The extent of the interference from the lanthanoids and yttrium on the determination of europium, samarium, and terbium was tested across the widest possible analytical range, since Sen Gupta3 has mentioned that interference can be overcome by dilution. (The dilution effect is commonly used to overcome interference in flame systems. The principle of this involves reduction of the total number of atoms in the light path, although the ratio of interferent to analyte does not change.)

Ratios of interferent to analyte of 100, 50, and 10:1 were used in the experiments, each interferent being added individually to the analyte. This was done in an attempt to simplify the experiments, since it was thought that the use of mixtures of the interferents would only complicate and prolong the investigation. It was found that an increase in the ashing temperature to 1000 °C for terbium and europium and to 1200 °C for samarium reduced some of the interference effects from the other lanthanoids, and did not significantly decrease the sensitivity for the analytes in the absence of the interferents.

2.6.2.1. Interference Effects on Europium

The effect of interference from lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and yttrium was tested at ratios of interferent to analyte of 100, 50, and 10:1, the amounts of europium atomized being 0.5 ng, 1.0 ng, 1.5 ng, 2.0 ng, and 2.5 ng. The effect of the interference on the analytical peak height was determined as the percentage enhancement or suppression of the original peak (i.e. the peak in the absence of the interferent). A 10 per cent margin of error was allowed in the measurement of the analytical peaks, and each peak was measured at least twice.

The europium peaks were not appreciably enhanced or suppressed by the elements tested. In the presence of a hundredfold excess of elements like samarium and ytterbium, there was some broadening of the peak, but the peak height remained within the 10 per cent margin of error. However, large amounts of the more-refractory lanthanoids reduced the usable life of the graphite furnace, and under those conditions the tube had to be replaced more frequently than usual.

2.6.2.2. Interference Effects on Samarium

The effect of interferences from lanthanum, cerium, praseodymium, neodymium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and yttrium was tested at ratios of interferent to analyte of 100, 50, and 10:1, the amounts of samarium atomized being 2.5 ng, 5.0 ng, 7.5 ng, 10.0 ng, and 12.5 ng. The effect of the interference was determined in the same manner as that described for europium.

No interference was noted from lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium, dysprosium, holmium, erbium, and yttrium at the ratios employed. However, interference from europium, thulium, and ytterbium at ratios of 50 and 100:1 resulted in suppression of the atomization peak height of less than 20 per cent. The effects of the presence of europium, thulium, and ytterbium on the calibration curve for samarium are shown in Figure 4. As can be seen, these interferences can be overcome by dilution of the sample solution, since they are less severe at low concentrations. It is interesting that the elements that interfere in the samarium response are, like samarium, the more-volatile lanthanoids; hence, an interference mechanism based on this phenomenon can be postulated. If the atomization of these
more-volatile species generates more of the interferent in the vapour phase, then it is possible that some type of mixed compound is being formed and that, consequently, less samarium atoms are present in the vapour phase, and hence are available for measurement. Alternatively, if atomization in all instances is due to thermal dissociation of the oxide, then perhaps the excess quantity of oxygen present, due to the dissociation of the monoxides of thulium, ytterbium, and europium, causes the recombination of samarium monoxide in the vapour phase. Samarium monoxide is more stable than the oxides of thulium, europium, and ytterbium, but less stable than the oxides of the other lanthanoids.

![Graphs showing effect of interference of europium, ytterbium, and thulium on calibration curve for samarium](image)

(i) Sm calibration in the absence of the interferent
(ii) Sm calibration in the presence of the interferent

FIGURE 4. Effect of the interference of europium, ytterbium, and thulium on the calibration curve for samarium
2.6.2.3. Interference Effects on Terbium

Interference on terbium from lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and yttrium was established at ratios of 100, 50, and 10:1. The amounts of terbium atomized were 25, 50, 75, 100, and 125 ng. The effect of the interferent was determined in the same manner as that described for europium.

Severe interferences from all the lanthanoids occurred even at a ratio of interferent to analyte of 10:1. The interferences followed two distinct patterns. Samarium, thulium, ytterbium and europium all caused suppression (of less than 50 per cent) of the terbium response, an effect that increased with increasing terbium concentration (i.e. the normal dilution effect). The other lanthanoids caused enhancement of the terbium response, which was more pronounced at lower concentrations of terbium. In solutions containing 25 ng of terbium, this enhancement exceeded 100 per cent in the presence of a fiftyfold excess of dysprosium, erbium, or gadolinium. However, in solutions containing 125 ng of terbium, the enhancement was only 50 per cent in the presence of the same interferents at the same relative concentrations.

An attempt was made to determine the interference mechanism in each of the above-mentioned cases. For simplicity, erbium was chosen as an example of the interferents causing enhancement, and samarium as an example of the interferents causing suppression.

(1) Interference from Erbium on Terbium

In this experiment, the erbium concentration was kept constant and the erbium concentration was varied, 100 ng of terbium being atomized in the presence of 2, 5, 10, 100, 1000, 2000, 5000, and 10 000 ng of erbium, corresponding to ratios of erbium to terbium of 1:50, 1:20, 1:10, 1:1, 10:1, 20:1, 50:1, and 100:1 respectively (i.e. from excess terbium to excess erbium). The peak heights obtained on the atomization of these mixtures were compared with a peak height obtained for terbium alone, a larger or smaller peak being taken as an indication of enhancement or suppression respectively. As the reproducibility was good, each peak was measured only twice. The results of this experiment are represented diagrammatically in Figure 5. An examination of this diagram shows that, at ratios of erbium to terbium from 1:1 to 20:1, the terbium peak height increases dramatically whereas, at ratios of 50:1 and 100:1, it decreases significantly. Although this effect cannot be explained without difficulty, it is possible that, initially, the addition of these lanthanoids causes more terbium to be released as the element during atomization, but that the effect is nullified at higher concentrations.

(2) Interference from Samarium on Terbium

The interference from samarium was tested in the same manner as that from erbium, 100 ng of terbium being atomized in the presence of 2, 5, 10, 100, 1000, 2000, 5000, and 10 000 ng of samarium, corresponding to ratios of samarium to terbium of 1:50, 1:20, 1:10, 1:1, 10:1, 20:1, 50:1, and 100:1 respectively. The atomization peak heights obtained in the presence of samarium and in its absence were compared, and it was found that an increase in the amount of samarium present was accompanied by a corresponding increase in the height of the terbium atomization peak. At a ratio of samarium to terbium of 100:1 there appears to be a decrease in terbium sensitivity. However, when this peak height is compared with that obtained for the atomization of terbium alone, the overall effect is one of enhancement (Figure 6). It was thought that this effect could be due to some kind of background noise or spectral overlap. Therefore, these mixtures were measured again under the same conditions except that the background was corrected by use of a deuterium background-correction system. The results seemed to indicate that, up to ratios of 1:1, the height of the terbium atomization peak was not influenced by the samarium present. However, large negative, overcompensated peaks were obtained in the presence of higher concentrations of samarium, which suggests that the deuterium background-correction system could not correct for the background present.

It was found that, at the terbium wavelength and when a terbium hollow-cathode lamp was used, varying quantities of samarium, atomized from the furnace, gave rise to absorbance values that exhibited the characteristics of a calibration curve. This suggested that some sort of spectral overlap was occurring. This means that, if the interference from samarium on terbium is to be overcome, the terbium and the samarium will have to be separated.
3. RESULTS

Several samples were analysed so that the accuracy of the method could be determined. At the beginning of the present investigation, optimum conditions were established for twelve of the lanthanoids, and an attempt was made to determine as many of these as possible in the samples. Unfortunately, neither praseodymium nor neodymium could be determined, since the hollow-cathode lamps used at the beginning of the investigation were no longer available. Therefore, only the remaining ten lanthanoids, viz samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, were investigated.

The samples analysed were ‘in-house’ reference materials used at the Council for Mineral Technology (Mintek), viz NIM 66/69 (a high-grade monazite from the Vanrhynsdorp area), NIM 39/70 (a low-grade monazite from the Richards Bay area), NIM 50/71 (a medium-grade monazite made by the mixing of one part of NIM 66/69 to two parts of NIM 39/70), NIM 18/69 (a carbonatite from South West Africa), and NIM 35/71 and 36/71 (two syenite rocks). Although recommended values are not available for all the lanthanoids in these samples, a set of preferred values for the lanthanoids in NIM 66/69, NIM 39/70, and NIM 50/71 had been established previously. Furthermore, the analytical results for the lanthanoid elements, although not sufficiently numerous for statistical evaluation, have been recorded. The analytical method used is detailed in the Appendix. As an increase in the ashing temperatures had been necessary when terbium,
DETERMINATION OF LANTHANOID ELEMENTS

FIGURE 6. Interference effect of samarium on terbium at various ratios of interferent to analyte

Samarium, and europium were measured in the presence of the other lanthanoids, it was decided that the ashing temperature should be increased to 1000°C throughout.

The analyses of these samples are given in Tables 4 to 6. The 'other' results used for comparison are very variable, but they are the best available, and very few international reference materials have recommended values for all the lanthanoids. From this comparison, it appears that the lanthanoids can be divided into three distinct groups for analysis by electrothermal atomization.

The first group consists of lanthanoids that can be measured in most types of samples by direct calibration (i.e. by the measurement of a set of standards, the plotting of a graph of concentration versus peak height, and calculation of the concentration of analyte in the sample from the graph). These are samarium, europium, thulium, and ytterbium (Table 4).

The next group consists of those elements for which the interference during the measurement by direct calibration can be overcome by the method of analyte additions, viz dysprosium, holmium, and erbium (Table 5).
## TABLE 4

Analyses for samarium, europium, thulium, and ytterbium in reference materials

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<thead>
<tr>
<th>Element</th>
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<th>NIM 50/71</th>
<th>NIM 18/69</th>
<th>NIM 35/71</th>
<th>NIM 36/71</th>
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<td>B</td>
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A = Results by the direct method
B = Results by the method of analyte additions
C = 'Other' results (not certified)
### TABLE 5

**Analyses for dysprosium, holmium, and erbium in reference materials**

<table>
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<tr>
<th>Element</th>
<th>NIM 66/69</th>
<th>NIM 39/70</th>
<th>NIM 50/71</th>
<th>NIM 18/69</th>
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<th>NIM 36/71</th>
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<td>C</td>
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<td>C</td>
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<td>mg/g</td>
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<td>5.1</td>
<td>7.5</td>
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<td>79, 596</td>
<td>809, 973</td>
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<td>Holmium</td>
<td>mg/µg</td>
<td>mg/µg</td>
<td>mg/µg</td>
<td>µg/µg</td>
<td>µg/µg</td>
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<td>1000</td>
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<td>399, 570</td>
<td>79, 129</td>
<td>88, 124</td>
<td>197, 237</td>
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<td>Erbium</td>
<td>mg/g</td>
<td>mg/g</td>
<td>mg/g</td>
<td>mg/g</td>
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<td>132, 247</td>
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<td>657</td>
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A Results by the direct calibration method
B Results by the method of analyte additions
C 'Other' results (not certified)
### TABLE 6

**Analyses for gadolinium, terbium, and lutetium in reference materials**

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<th>Element</th>
<th>NIM 66/69</th>
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<th>NIM 50/71</th>
<th>NIM 18/69</th>
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<td>B</td>
<td>C</td>
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<tr>
<td>Gadolinium</td>
<td>mg/g</td>
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<td>mg/g</td>
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<td>1.4, 0.8</td>
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<td>8.2, 7.2</td>
<td>8.5, 7.8</td>
<td>1.5, 1.4</td>
<td>1.2, 1.3</td>
<td>3.4, 3.1</td>
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<td>Terbium</td>
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<td>µg/g</td>
<td>µg/g</td>
<td>µg/g</td>
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<td>816</td>
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<td>881, 632</td>
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<td>163, 128</td>
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<td>599, 1700</td>
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<tr>
<td>Lutetium</td>
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<td>763</td>
<td>332</td>
<td>40, 16, 89</td>
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</tr>
</tbody>
</table>

A: Results by the direct calibration method
B: Results by the method of analytic additions
C: 'Other' results (not certified)
DETERMINATION OF LANTHANOID ELEMENTS

The last group consists of the elements that cannot be measured by electrothermal atomization with any real degree of precision or accuracy, viz terbium, gadolinium, and lutetium (Table 6). Terbium and lutetium are both subject to severe interference in the presence of the other lanthanoids. Although the results for gadolinium in NIM 66/69, 39/70, and 50/71, which were obtained by the method of analyte additions, were comparable with the 'other' results, the results for NIV 18'69, 35/71, and 36/71 were not very good. Furthermore, the reproducibility of the measurement of gadolinium in these samples was poor; gadolinium was therefore included in the third group.

4. DISCUSSION

Different interference effects were found for the three lanthanoids investigated (europium, samarium, and terbium). This information is useful in the analysis of these elements and can also be used as a basis for the postulation of interference mechanisms for the other lanthanoids. Europium should be determined easily in samples containing even a hundredfold excess of the other lanthanoids. Similarly, ytterbium, which has a similar vapour pressure and monoxide bond-dissociation energy, would be expected to be relatively free from interference. Samarium suffered interference from the other volatile lanthanoids at ratios of interferent to analyte of more than 50:1. Therefore, it should be possible for samarium to be measured in the presence of these other lanthanoids as long as that ratio is not exceeded. The characteristics of thulium, which is slightly less volatile but has a lower monoxide bond-dissociation energy, may be similar to those of samarium. Terbium, however, is subject to severe interference from the other lanthanoids. This interference is due in some instances to spectral effects and in others to chemical effects. It is therefore impossible for terbium to be measured by ETA-AAS in samples also containing the other lanthanoids, and the terbium has to be separated, for example by ion-exchange chromatography, prior to measurement. Terbium is one of the more-refractory lanthanoids and also has a high monoxide bond-dissociation energy. Lutetium, gadolinium, lanthanum, cerium, praseodymium, and possibly neodymium, which are also very refractory and have high monoxide bond-dissociation energies, may also be subject to severe interference. This leaves dysprosium, holmium, and erbium, whose vapour pressures and monoxide bond-dissociation energies lie between those of terbium and samarium. The interference effects in their determination may therefore be less severe than in that of terbium, but more severe than in that of samarium.

5. SUMMARY

The measurement of selected lanthanoid elements by ETA-AAS led to the establishment of optimum ashing and atomization temperatures for twelve of the lanthanoids, viz neodymium, praseodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Calibration curves and analytical precision were also established.

The results of the tests on terbium, samarium, and europium by a variety of techniques indicated that the atomization behaviour of samarium and europium is not dissimilar, but that the atomization characteristics of terbium are quite different.

The interference effects on these three lanthanoids from increasing quantities of hydrochloric and nitric acids were found to be most severe in the determination of terbium, and the samarium response was also suppressed by excess quantities of nitric acid. Interelement interferences were tested across the calibration range for each of the analytes, and at ratios of interferent to analyte of 10, 50, and 100:1 there was no interference on the europium response. The samarium response was suppressed in the presence of excess europium, ytterbium, and thulium, but this interference can be overcome by dilution since it is more severe at higher concentrations of samarium. The interference in the determination of terbium was severe, all the other lanthanoids either suppressing or enhancing the terbium response to some extent. Hence, the interference on terbium is not easily overcome, and some sort of separation of the terbium from the other lanthanoids is necessary prior to measurement.

The lanthanoids were measured in six 'in-house' Mintek reference materials after they had been separated from the sample matrix by ion exchange. The results obtained show that there are three groups of lanthanoids in terms of their determination in this type of material. The first group consists of those elements for which the determination is relatively uncomplicated, viz samarium, europium, ytterbium, and thulium; the second group comprises those elements for which the method of analyte additions is necessary, viz holmium, erbium, and dysprosium; and the third group consists of those elements that cannot be measured with any degree of accuracy because the interference is too severe, viz terbium, lutetium, and gadolinium.
6. REFERENCES


DETERMINATION OF LANTHANOID ELEMENTS

APPENDIX

DETERMINATION OF SAMARIUM, EUROPIUM, THULIUM, AND YTTERBIUM IN SILICATE ROCKS BY
ATOMIC-ABSORPTION SPECTROSCOPY USING ELECTROTHERMAL ATOMIZATION
(LABORATORY METHOD NO. 0/25)

1. OUTLINE

After fusion with potassium bifluoride, the insoluble lanthanoid and calcium fluorides are filtered off and dissolved. After the lanthanoids have been separated from calcium and the base metals on a cation-exchange resin, they are measured by atomic-absorption spectroscopy using electrothermal atomization.

2. APPLICATION

The method is applicable to the measurement of samarium, europium, thulium, and ytterbium in samples of silicate rocks at concentrations so low that they preclude measurement by less sensitive techniques. For 1 g of sample made up to 25 ml, the lower limits of determination are 3 μg/g for samarium, 0.05 μg/g for europium, 0.1 μg/g for thulium, and 0.02 μg/g for ytterbium.

The total time taken for the analysis of one sample is 3 days, and that for 10 samples is 7 days.

3. APPARATUS

The following apparatus is required: a Varian AA1475 atomic-absorption spectrophotometer fitted with simultaneous background correction, a GTA-95 furnace system, a two-pen chart recorder (JJ Instruments CR652S), and a printer (Epson MX80).

4. REAGENTS

(1) Hydrochloric Acid, 37 per cent
    A.R. grade.

(2) Hydrochloric Acid, 1.85 M
    Dilute 231 ml of 12 M hydrochloric acid to 1500 ml with water.

(3) Hydrochloric Acid, 4 M
    Dilute 666 ml of 12 M hydrochloric acid to 2000 ml with water.

(4) Hydrofluoric Acid, 1 per cent (v/v)
    Transfer 400 ml of water to a plastic bottle, add 4 ml of hydrofluoric acid, and mix.

(5) Cation Resin
    Bio.Rad AG 50W X8 (200 to 400 mesh), hydrogen form.

(6) Samarium, Europium, and Thulium Stock Standard Solutions, 1000 mg/l
    Dissolve 1.1579 g of Spec-pure Eu₂O₃, 1.159 g of Spec-pure Sm₂O₃, and 1.142 g of Spec-pure Tm₂O₃ each in the minimum volume of 1:1 hydrochloric acid, and dilute to 1 litre with distilled water.

(7) Ytterbium Stock Standard Solution, 1000 mg/l
    Dissolve 1.139 g of Spec-pure Yb₂O₃ in 20 ml of 37 per cent hydrochloric acid, and dilute to 1 litre with distilled water.

(8) Diluted Stock Standard Solutions
    Dilute stock standard solutions to the following appropriate range of concentrations with 1 per cent (v/v) hydrochloric acid: samarium 0 to 1.0 mg/l, europium 0 to 0.25 mg/l, thulium 0 to 0.05 mg/l, and ytterbium 0 to 0.025 mg/l.
5. CONDITIONS FOR MEASUREMENT

The conditions for measurement with the Varian GTA-9S system are set out in Table 1-1.

**TABLE I-1**

*Conditions for the measurement of samarium, europium, thulium, and ytterbium with the Varian GTA-9S system*

<table>
<thead>
<tr>
<th>Element</th>
<th>Lamp current mA</th>
<th>Slit width nm</th>
<th>Wavelength nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samarium</td>
<td>8</td>
<td>0.2</td>
<td>429.67</td>
</tr>
<tr>
<td>Europium</td>
<td>8</td>
<td>0.2</td>
<td>459.40</td>
</tr>
<tr>
<td>Thulium</td>
<td>10</td>
<td>0.2</td>
<td>371.79</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>15</td>
<td>0.2</td>
<td>398.80</td>
</tr>
</tbody>
</table>

The furnace-operating conditions are set out in Table 1-2.

**TABLE I-2**

*Furnace-operating conditions for the measurement of samarium, europium, thulium, and ytterbium with the Varian GTA-9S system*

<table>
<thead>
<tr>
<th>Step no.</th>
<th>Temperature °C</th>
<th>Time s</th>
<th>Gas flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>5.0</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>95</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>1000</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>7*</td>
<td>2700</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8*</td>
<td>2700</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>2850</td>
<td>0.0</td>
<td>3.0</td>
</tr>
<tr>
<td>10</td>
<td>2850</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* Peak measured

6. PROCEDURE

6.1. Fusion of the Sample

a. Transfer 1 g of finely ground sample into a platinum crucible. Place the crucible in a muffle furnace and heat to 900 °C for 10 minutes. Cool.
b. Carefully fuse the residue in the crucible with potassium bifluoride, using 1 g of potassium bifluoride for each 0.1 g of sample taken. Place the crucible over a low flame, and gradually increase the heat of the flame. Fuse over a full flame until the melt is a clear red-hot molten mass. As the melt cools, swirl it so that it forms a thin coating on the sides of the crucible.
c. Transfer the cold crucible to a 250 ml plastic beaker and add 180 ml of hot water. Add 20 ml of hydrofluoric acid. Using a pipette, add 0.5 ml of hydrochloric acid, and mix with a plastic rod.
d. Digest on a steam-bath with occasional stirring until the soluble salts have been completely dissolved and the lanthanoid fluorides have been precipitated. Remove the crucible and rinse.
e. Digest on a steam-bath for 2 hours and cool. Add 0.5 g of cellulose powder, stir, and filter through a no. 42 Whatman filter paper, using a plastic funnel and beaker. Wash eight times with cold 1 per cent hydrofluoric acid solution, and finally rinse with water.

f. Transfer the filter paper and precipitate to a 400 ml squat beaker. Add 20 ml of nitric acid and 5 ml of perchloric acid, cover with a watch-glass, and transfer the beaker to a hot-plate. Bring to fumes of perchloric acid. Cool, rinse the cover and sides of the beaker, and evaporate to a moist state. (Note 1.)

g. Remove the watch-glass and evaporate just to dryness. Add 5 ml of hydrochloric acid down the sides of the beaker, and evaporate just to dryness. Repeat the addition of hydrochloric acid and evaporation five times. Cool.

h. Add 6 ml of hydrochloric acid, and dilute to 100 ml. Warm to dissolve the salts. (Note 2.)

6.2. Separation of the Lanthanoids

a. Prepare a cation-exchange column by placing 45 ml of AG 50W-X8 resin (200 to 400 mesh) in a borosilicate-glass column 30 cm long and 2 cm in internal diameter, and having a no. 2 sintered-glass disc. Rinse the column with water and allow it to drain.

b. With the aid of a glass rod, carefully run the sample solution down the sides of the column, taking care not to disturb the surface of the resin. Allow the solution to drain into the column. Wash the sides of the column twice with water without disturbing the surface of the resin, and allow the column to drain each time. (Note 3.)

c. Elute the sample impurities with 300 ml of 1.85 M hydrochloric acid, carefully adding the eluant with the aid of a glass rod. Allow to drain, and reject the eluate.

d. Elute the lanthanoids with 400 ml of 4 M hydrochloric acid, and collect the eluate in a 500 ml beaker. Allow to drain. (Note 4.)

e. Reduce to a small volume on a hot-plate, and make up to 25 ml with water. The acid concentration should be 1 per cent.

6.3. Measurement of Samarium, Europium, Thulium, and Ytterbium

a. Set up the GTA-95 for each element in turn.

b. Measure each of the calibration standards, using the autosampler to transfer 25 µl aliquot portions of each standard to the graphite furnace. Make at least two measurements of each standard and, if the difference between the successive absorbance measurements is greater than 10 per cent, take another measurement.

c. Measure the blank solution and the sample solution in the same way, diluting the sample solution if necessary.

d. Calculate the concentrations of the analytes in the sample from the calibration graph (or use a computer with a suitable programme), as follows:

\[
\text{Analyte in sample, } \mu g/g = \frac{\text{Concn (from calibration graph)} \times \text{dilution volume}}{\text{Mass taken}}
\]

7. NOTES

(1) If the perchloric acid turns dark brown, cool it slightly, add more nitric acid, and evaporate to fumes again.

(2) If the salts do not all dissolve, decant the solution and add 3 ml of hydrochloric acid and 50 ml of water to the undissolved salts. Warm to dissolve. If necessary, dilute the sample solution further to achieve dissolution, but ensure that the concentration of hydrochloric acid does not exceed 6 per cent.

(3) Ensure that the resin is not disturbed during the addition of solution or during washing, since channelling, which would lower the efficiency of the resin, may result.

(4) To clean the AG 50W-X8 (200 to 400 mesh) cation resin, wash it with 300 ml of 1:1 hydrochloric acid, and allow to drain. Wash thoroughly with water, agitating the resin by shaking the column and allowing it to resettle. After being washed, the resin should have a pH value of approximately 6.