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A RAPID ROUTINE METHOD FOR THE DETERMINATION OF SUB-MICROGRAM AND MICROGRAM AMOUNTS OF BERYLLIUM IN FILTER PAPER

by

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SUMMARY

A rapid routine method for the determination of sub-microgram and microgram amounts of beryllium in filter paper smears is presented. Beryllium is determined fluorometrically with 3:5:7:2':4'-pentahydroxyflavone (MORIN). Many interfering elements are removed by adsorption on a strongly basic anion-exchange resin from 9M hydrochloric acid.

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INTRODUCTION

Due to the high toxicity of beryllium and its increasing use as a nuclear material, the determination of traces of this element is growing in importance. A need exists for a rapid method for the routine determination of submicrogram quantities of beryllium. A method is presented in this paper which allows twenty filter paper smears to be analysed for beryllium in less than six hours.

Sodium hydroxide solutions of beryllium fluoresce strongly with 3:5:7:2':4' - pentahydroxyflavone (MORIN)[1]. This reaction provides by far the most sensitive chemical method at present available for the determination of beryllium[2]. Beryllium may be detected at a concentration as low as 5×10^{-4} p.p.m., and 5×10^{-3} p.p.m. may be measured with a precision comparable with normal spectrophotometric procedures. The method is, however, subject to many interferences[3], and a preliminary separation of beryllium is usually necessary. The separation has often been accomplished by precipitation of the beryllium as hydroxide or phosphate, using aluminium or iron carrier, followed by a mercury cathode electrolysis [2,4,5]. These procedures are too time-consuming for routine use. Several cation-exchange separations of beryllium have been described [6,7] and a method by Nadkarni, Varde and Athavale[8], for the determination of beryllium in ores, was modified in this laboratory for use in the separation of trace amounts of this element. However, these cation-exchange procedures were rejected in favour of a more rapid anion-exchange separation from 9M hydrochloric acid. Many metals are retained by a strongly-basic anion-exchange resin from 9M HCl[9], whereas beryllium is not, and passes into the effluent. Most foreign elements which also escape the anion-exchange separation do not interfere, or their interference may be removed by complexing with ethylene diamine tetra acetic acid (E.D.T.A.).

APPARATUS

A Hilger "Uvispek" spectrophotometer with fluorimeter attachment was used for all fluorescence measurements. The exciting radiation is provided by a 36W filament lamp, and the sample cells are of 18ml capacity. A 365mμ filter was used to isolate the exciting radiation.

Ion-exchange column.

A simple U-tube type ion exchange column[10] was used, of length 4.5" and 0.25" in diameter, while the lead-off capillary tube had an internal diameter of 0.125". A glass-wool plug was used to support the resin, and a 50ml separatory funnel was attached to the top of the column with a $\neq$ B7 joint. The flow-rate was easily controlled by the stop-cock of the separatory funnel. This ion-exchange apparatus is very simple and cheap to construct, and it is convenient in routine work to have a number of such columns arranged in series, so that one column is available per sample.

Ion-exchange resin.

De-Acidite FF. From the Permutit Co., Ltd. London.

REAGENTS

1% sodium stannite solution –

Dissolve 1g of stannous chloride dihydrate in 100ml of 1.25N sodium hydroxide by warming gently on a water bath with continuous stirring. This solution must be prepared fresh daily.

0.025% Morin solution -

B.D.H. grade 3:5:7:2':4' - pentahydroxyflavone was used without further purification. Dissolve 0.25g in 1l. of 95% ethanol. Store in a refrigerator.

Quinine sulphate stock solution -

Dissolve 0.125g of quinine sulphate in 250ml of water. Add 10ml of 2N H_2SO_4 and dilute to 2l. Store in a dark bottle.

All other chemicals used were of reagent grade.

PROCEDURE

Fill the ion-exchange column with water, then add De-Acidite FF, as a slurry in water, until the column contains about 2ml of resin. Place the separatory funnel in position and wash the resin first with 40ml of water, then with 40ml of 9M HCl.

Digest the filter paper smear in a small conical flask with 1ml of HNO_3 and 4ml of 72% $HClO_4$. Evaporate to complete dryness on a hot plate. Dissolve the residue by warming with 10ml of 9M Hcl. Cool, and pass the solution through the ion-exchange column at a rate of 1-2ml per minute. Wash with 40ml of 9M HCl and evaporate the effluent just to dryness. Dissolve the residue by warming with 5ml of water. Cool, and transfer to a 25ml volumetric flask. Dilute to the mark with water.

Pipette a suitable aliquot of the sample solution into a small beaker. Dilute to about 25ml with water. Add 1ml of 10% E.D.T.A. (disodium salt) and neutralise carefully with 10% NaOH, using indicator paper. Transfer the solution to a 50ml volumetric flask. Add 2ml of sodium stannite solution, mix, then 1ml of morin solution. Dilute to volume with water. Prepare a blank in the same manner, substituting water for the sample aliquot. Dilute 2ml of the quinine sulphate solution to 50ml in a volumetric flask.

Determine the fluorescence after 15 min and before 60 min by setting the quinine sulphate solution at zero absorbance, then measuring the absorbance of the blank and sample solutions. The Δ absorbance value (blank absorbance minus sample absorbance) may then be related to beryllium concentration from a calibration curve. The beryllium content of a blank filter paper, and of the acids used for digestion is usually less than 0.03 μg.

BERYLLIUM RECOVERY

Known amounts of beryllium were subjected to the ion-exchange separation. Table I shows that excellent recoveries may be obtained.

TABLE I.

BERYLLIUM RECOVERY

Be taken (μg)	Be found (μg)	% Recovery
0.016	0.015	94
0.040	0.044	110
0.240	0.235	98
0.400	0.400	100
0.800	0.775	97
4.00	3.88	97

SENSITIVITY OF THE METHOD

Less than 0.05 µg of beryllium in a paper smear may be detected. Laitinen and Kivalo[5] recommend adding 1M sodium sulphate or 2M sodium chloride to enhance the beryllium fluorescence. Sodium sulphate was found to be difficult to use at these concentrations due to its relatively low solubility, and 1.5M sodium chloride, at the morin concentration used, actually depressed the fluorescence slightly. In addition, the fluorescence of solutions containing large concentrations of sodium chloride faded much faster than those without added salt. Using the procedure above, the fluorescence showed no appreciable fading for 60 min. A morin concentration of 5×10^{-4}% in 0.05M NaOH was found to be optimum for maximum fluorescence.

EFFECT OF DIVERSE IONS

Table II shows the effect of some common cations which were added to a known amount of beryllium and the determination carried out as in the procedure above.

It may be seen that thorium and chromium are the only serious interferences. Copper, zinc, iron and uranium are removed by the ion-exchange column. Calcium and nickel are effectively complexed by E.D.T.A., and aluminium does not interfere in sodium hydroxide solution.

THORIUM

Thorium is not retained by De-acidite FF from 9M HCl.[9] and does not form a strong complex with E.D.T.A. in alkaline solution.

If more than 500 µg of thorium is present in the final solution a precipitate of hydrated thorium oxide forms on the addition of sodium stannite reagent. Low results are then obtaine, probably due to co-precipitation of beryllium. Smaller amounts of thorium do not precipitate, and the fluorescence of the solution is then enhanced, leading to high beryllium results. Using the recommended procedure, the maximum permissible concentration of thorium, for an error of less than 5%, is 80 times the beryllium concentration. The use of pyrophosphate, as recommended by Sandell,[3], did not remove the interference of thorium.

CHROMIUM

Chromium interferes seriously, since chromite ion is formed in sodium hydroxide solution, and this appears to strongly absorb U.V. radiation. Chromium (III) was found to be only very weakly adsorbed on De-acidite FF from 9M HCl. Chromium (VI) is strongly adsorbed from 1 – 2 M HCl, but is quantitatively reduced to the lower valency by 9M HCl. The maximum concentration of chromium permissible is 100 times the beryllium concentration.

TABLE II

EFFECT OF DIVERSE IONS

0.400 µg of Be taken in each case.

Ion added.	Amount Added mg.	Be found µg.	Relative Error %
Ca^{+2}	1.0	0.420	+5
Ni^{+2}	1.0	0.421	+5
Al^{+3}	1.0	0.385	–4
Cu^{+2}	1.0	0.377	–6
Zn^{+2}	1,0	0.388	–3
Pb^{+2}	1.0	0.400	0

TABLE II CONT'D

Ion added.	Amount Added mg.	Be found μg.	Relative Error %
Fe^{+3}	5.0	0.393	–2
U^{+6}	1.0	0.394	–2
Th^{+4}	1.0	0.248	–38
Th^{+4}	0.5	0.340	–15
Th^{+4}	0.1	0.520	+30
Th^{+4}	0.02	0.402	0
Cr^{+3}	0.5	0.041	–90
Cr^{+3}	0.25	0.128	–68
Cr^{+3}	0.05	0.387	–3

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