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SPECTROPHOTOMETRIC DETERMINATIONS OF BERYLLIUM AND FLUORIDE USING CHROME AZUROL S

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ABSTRACT

Chrome Azurol S has been applied to the spectrophotometric determination of beryllium and fluoride. The colored beryllium—Chrome Azurol S complex is formed at pH 6.0 in the presence of a pyridine—hydrochloric acid buffer, which enhances the sensitivity of the dye to beryllium and increases the sensitivity of the metal-dye complex to fluoride. With the procedure described, from 1 to 30 μgm of fluoride per 50 mℓ volume can be determined to a precision of 1 μgm, and from 0.2 to 10 μgm of beryllium per 50 mℓ volume can be determined to a precision of 0.2 μgm. Studies were made on the variables of the system, on the interferences, and on an ion exchange method to separate uranium from beryllium.

I. INTRODUCTION

The volume of methods reported for the determination of microgram amounts of fluoride shows that the determination is difficult and is not completely satisfactory. Fluoride is best determined spectrophotometrically by its bleaching action on metal-dye colored complexes and a great variety of metals and dyes have been used for this purpose[1-6] including the aluminum—Chrome Azurol S complex.[1] Willard and Horton[7] report that Chrome Azurol S is one of the most sensitive indicators for the titration of fluoride using thorium.

Beryllium also forms a strong complex with fluoride and it seemed that beryllium might have advantages as a Chrome Azurol S complex for the determination of fluoride. Theis[8] and Wood[9] used Chrome Azurol S as a sensitive indicator for the determination of small amounts of beryllium.

Chrome Azurol S, the sodium salt of 3''-sulfo-2'', 6''-dichloro-3, 3'-dimethyl-4-hydroxy-fuchson-5, 5'-dicarboxylic acid, is also known as Solochrome Brilliant Blue B, Polytrop Blue R, and has the British Colour Index No. 723. In weakly acidic beryllium solution, the dye forms a pink to purple-blue color which is bleached by the presence of fluorides.

The investigation of a method for fluoride in this laboratory was initiated by the need to analyze for microgram amounts of fluoride in enriched uranium sulfate which is used as the fuel in water-boiler type nuclear reactors. A commercial preparation of uranium sulfate for reactor fuel necessitates its conversion from the uranium hexafluoride and some fluoride would be expected in the sulfate salt. As fluoride in acid solution speeds the corrosion of stainless steel vessels, the quantity of fluoride present, however small, must be known. The determination of fluoride in uranyl sulfate solution is therefore, important.

The investigation of the beryllium—Chrome Azurol S complex for the determination of fluoride, led to the development of a method for the determination of microgram quantities of beryllium using this dye.

This paper describes the optimum conditions for the development of the beryllium—Chrome Azurol S colored complex, the use of an amine buffer, the stability of the complex, interferences with and methods for the determination of both fluoride and beryllium in microgram quantities.

II. REAGENTS

A. STANDARD BERYLLIUM SOLUTIONS

Dissolve 1 gm of beryllium metal in dilute (10 per cent) hydrochloric acid and dilute to 1 ℓ with distilled water. Make suitable dilutions to obtain solutions containing 1 and 10 μgm of beryllium per mℓ.

Precaution

It is recommended that all powdered beryllium compounds be handled in a hood, and that an aspirator mask be worn.

B. CHROME AZUROL S REAGENT (0.05 Per Cent)

Dissolve 0.50 gm of Chrome Azurol S (Geigy Chemical Co., Los Angeles, California) in 1 ℓ of distilled water which contains 2 gm of gum arabic powder. Allow the solution to stand several days, then filter and store in a brown bottle. The solution will be stable for several weeks.

C. PYRIDINE—HYDROCHLORIC ACID BUFFER (pH 6.0)

Slowly add 35 mℓ of concentrated hydrochloric acid to 215 mℓ of pyridine.

III. PROCEDURES

A. STANDARD FLUORIDE CURVE

The standard curve is prepared by pipetting aliquots containing from 0 to 30 μgm of fluoride into a series of 50-mℓ volumetric flasks. Water is added to bring the volume to about 40 mℓ, and an aliquot containing 10 μgm of beryllium is added to each flask. Three mℓ of 2 per cent hydroxylamine hydrochloride solution, 2 mℓ of pyridine hydrochloride buffer, and 1 mℓ of Chrome Azurol S reagent are added, while the contents of the flask are mixed after each addition. (The pH should be 6.0 at this point.) The solutions are made to volume with distilled water, and allowed to stand for 15 min. The absorbance is measured with a Beckman Model DU spectrophotometer in 5-cm cells at 575 mμ, using a reagent blank containing all reagents except beryllium and fluoride as the reference solution. A standard curve is drawn from these values.

B. FLUORIDE DETERMINATION

If interfering substances are present in the sample, a separation must be made. If necessary, the sample may be adjusted to pH 6 ± 0.5 with a minimum amount of hydrochloric acid or ammonium hydroxide. The procedure for the standard curve is then followed. The micrograms of fluoride present are obtained from the standard curve.

C. STANDARD BERYLLIUM CURVE

The standard curve for beryllium is prepared by pipetting aliquots containing from 0 to 10 μgm of beryllium into 50-mℓ volumetric flasks. Distilled water is added to bring the volume to 40 mℓ. The amounts of hydroxylamine hydrochloride, pyridine-hydrochloride buffer, and Chrome Azurol S are added, according to the procedure for fluoride, then the fluoride procedure is followed.

D. BERYLLIUM DETERMINATION

After the sample has been freed from interferences, the above procedure is followed to determine the beryllium present.

IV. EXPERIMENTAL RESULTS

A. pH AND BUFFER

According to Theis[8] and Wood[9], a neutral or weakly acidic solution is optimum for the formation of the beryllium—Chrome Azurol S complex. The present studies showed that at pH 5 to 6, the color due to the complex is at a maximum, while the absorbance of the dye is small. The peak of maximum absorbance varies with the changes in pH as does the color intensity (Fig. 1). With no buffer present, the complex, at pH 6 to 7, has its peak in the 540 mμ region, while at pH 5, the peak is in the 570 mμ region. Figure 1 indicates that the optimum pH is 5 to 6; therefore, the preliminary investigation was carried out in this pH range. It was found that pH 6 was optimum when the pyridine—hydrochloric acid buffer was used (Fig. 2). The pH is critical and should be maintained at 6.0 ± 0.1, since the intensity of the color varies with pH.

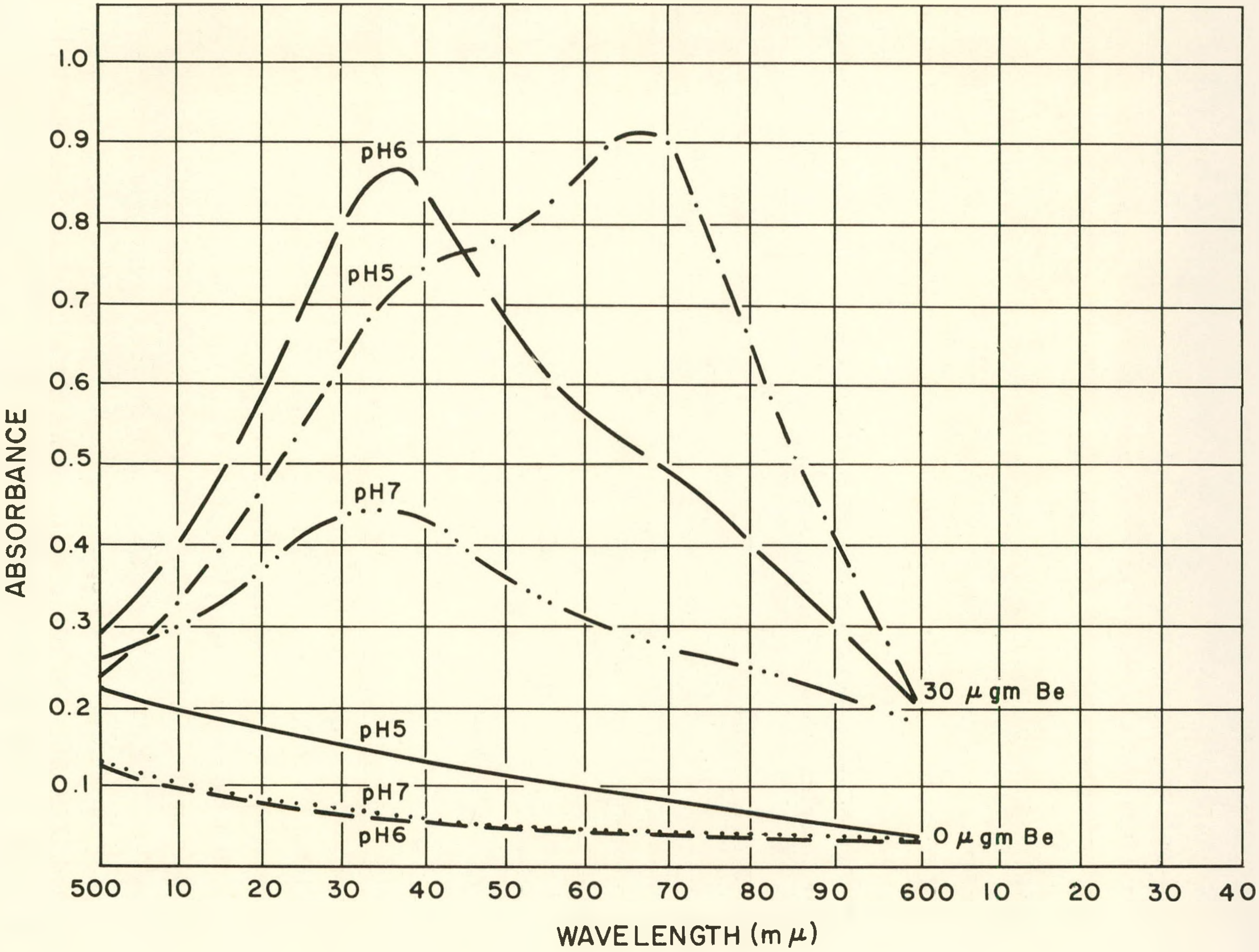

Fig. 1. Effect of pH on Beryllium—Chrome Azurol S with No Buffer Present

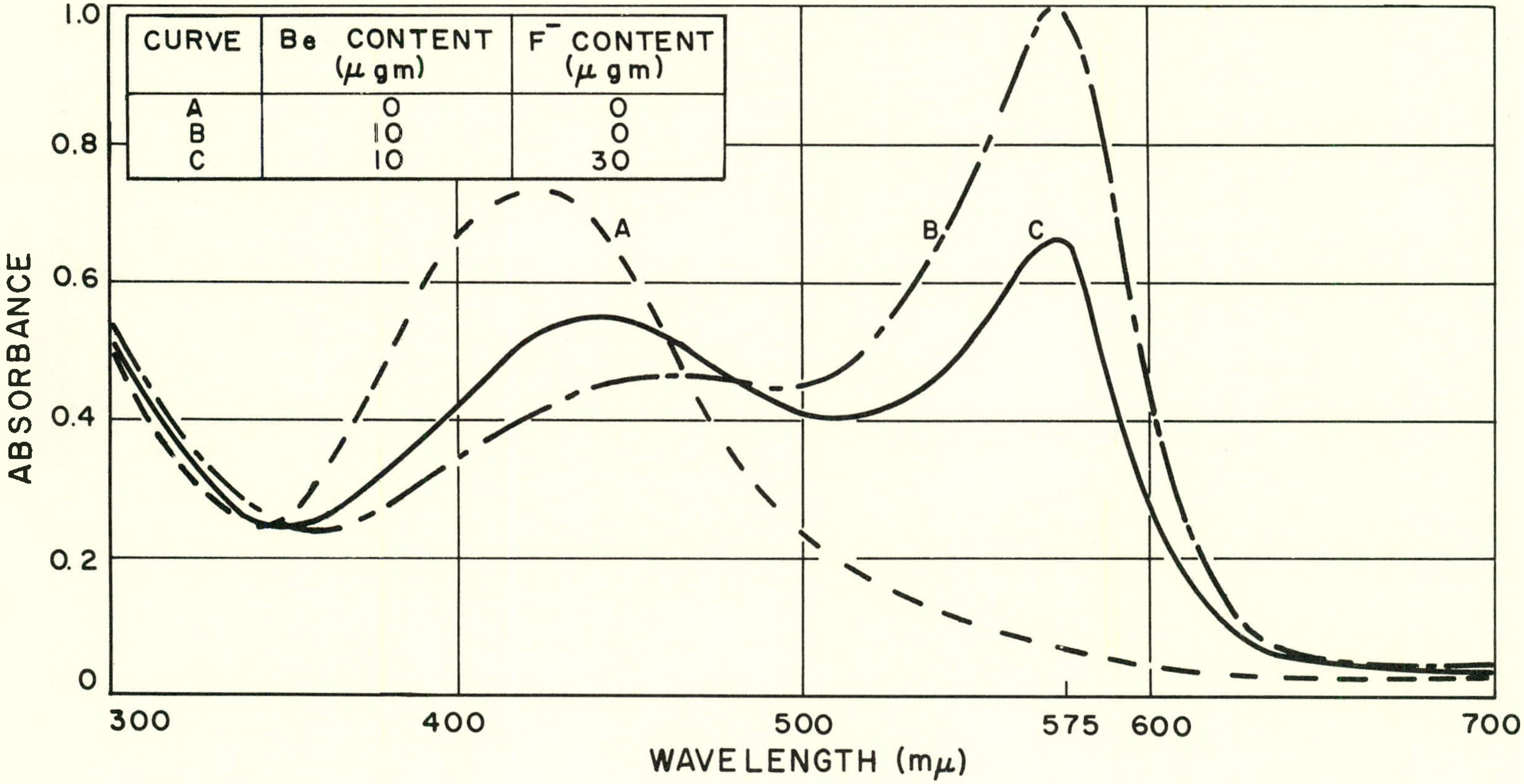

Fig. 2. Spectrophotometric Curves of the Beryllium—Fluoride—Chrome Azurol S System

Other workers[8,9] on the beryllium—Chrome Azurol S system maintained the desired pH values (pH 6 to 7) with acetate buffer; contrary to this, Revinson and Harley[6] reported that the thorium—Chrome Azurol S lake is bleached by carbonyl and carboxyl groups. They finally chose an amine (o-toluidine) as the buffer for a pH of 4.5. The preliminary investigations in this laboratory showed that the beryllium—Chrome Azurol S lake is also appreciably bleached by acetate and tartrate buffers. In addition to these buffers, others were tried. Whereas mannitol[10] has little effect on the color, it does not effectively buffer the solution. Hydrazine and hydrazine hydrochloride were used, but full color does not develop in the presence of this amine. When the pyridine—hydrochloric acid buffer was used, an enhancement of color intensity for the metal-dye complex was observed and good buffering was obtained.

Table I shows the effect of 2 mℓ of the pyridine buffer on 10 μgm of beryllium in a 50-mℓ volume with varying amounts of fluoride present. The pH was maintained at 6 in all tests. These solutions were measured in 1-cm cells, and the absorbance readings listed in the table were measured at the wave length of maximum absorbance at 575 mμ with pyridine present, and at 535 mμ in its absence. Pyridine enhances the intensity of the metal-dye complex and alternately the bleaching effect of the fluoride. The amount of pyridine buffer present must be kept reasonably constant to insure precise results, as a variance of 1 mℓ of buffer per 50 mℓ volume causes an optical density unit change of 0.04.

TABLE I

EFFECT OF PYRIDINE ON BERYLLIUM—CHROME AZUROL S COMPLEX

Pyridine Buffer (mℓ)	Fluoride (μ gm)	Wave Length (mμ)	Absorbance	Change in Absorbance
0	0	535	0.312	-
0	30	535	0.245	0.067
0	50	535	0.220	0.092
2	0	575	0.345	-
2	30	575	0.238	0.107
2	50	575	0.180	0.165

B. SPECTROPHOTOMETRIC CURVES

Figure 2 shows the spectrophotometric curves of the beryllium—fluoride—Chrome Azurol S system which were obtained by the standard curve procedure, except that 1-cm cells were used for the absorbance measurements. The dye alone has a low absorbance at 575 $m\mu$, whereas the beryllium—Chrome Azurol S complex has a maximum absorbance peak at this wave length. The addition of fluoride to the metal-dye lake bleaches the color and the decrease in absorbance is proportional to the fluoride concentration.

The standard curves for both beryllium and fluoride are linear and reproducible.

By the method of continuous variations[11] Chrome Azurol S was found to combine with beryllium in a mole ratio of 1 : 1.

C. COLOR STABILITY

The color of the metal-dye complex, even with fluoride present, is relatively stable for at least 5 hr when developed according to the standard curve procedure. During the first 15 min the absorbance readings decrease very slightly with fluoride present, and then remain constant. The optimum time for reading the samples is not critical, but if the samples are allowed to stand at least 15 min before reading, constant results are assured.

D. INTERFERENCES

The beryllium—Chrome Azurol S complex is subject to several interferences. Some of the substances which bleach the color (causing low results in the beryllium analysis and high results in the fluoride analysis) are shown in Table II. The extent of interference is given in terms of fluoride equivalent. In addition to the substances listed in Table II, acetate, versene, and fluoride also bleach the color of the beryllium—Chrome Azurol S complex. The concentration of these substances must be kept low.

Theis[8] reported that under the conditions he used, ferric iron, copper, aluminum, zirconium, and lead cause interference by forming colored complexes with the dye, and that the alkaline earth metals do not form violet compounds with the dye. Theis alleviated the iron effect with tartrate, the zirconium effect

TABLE II

INTERFERENCES WHICH BLEACH THE COLOR

Interference	Concentration (gm/50 mℓ)	F$^-$ Equivalent (μ gm)
NaCl	0.1	5
NH_4Cl	0.1	7
$(NH_4)_2SO_4$	0.1	12
$Na_2C_4H_4O_6 \cdot 2H_2O$	0.002	30
Na_2CO_3	0.02	7

by the addition of sodium fluoride, and the copper interference by Complexon; however, our studies clearly show that each of these additions (tartrate, fluoride, and Complexon) bleach the color of the beryllium—Chrome Azurol S lake when it is developed according to the procedure given in this paper. Wood[9] carried out semi-quantitative tests on possible interfering ions and found that Ni^{++}, Cu^{++}, Bi^{++}, Sn^{++}, Fe^{++}, Ti^{+3}, and Sb^{+3} interfere. Under the conditions described in this paper, uranium (VI) and iron (III), even when present in microgram quantities, from a blue color with the dye thus giving an interference. Investigation showed that the addition of 3 mℓ of 2 per cent hydroxylamine hydrochloride solution will not affect the beryllium—Chrome Azurol S color but will alleviate the interference caused by 1 mgm of iron or uranium. The addition of hydroxylamine hydrochloride is included in the standard procedure then, to insure freedom from interferences caused by small amounts of iron or uranium which may be present.

In general, however, to attain maximum sensitivity and to insure accurate results using the Chrome Azurol S method, all interfering ions must be removed. The removal of interferences in the determination of beryllium is discussed below (paragraph IIC 6). In analyzing for fluoride, the removal is usually accomplished by the distillation of the fluoride as the fluosilicic acid from a perchloric acid solution[6] or by the pyrohydrolysis method.[12]

E. DISTILLATION OF FLUORIDE FROM VARIOUS METALS

Studies were made to determine if microgram quantities of fluoride could be quantitatively distilled from 1 mgm each of aluminum, beryllium, zirconium, thorium, and iron. Two sets of distillations were made; one containing only the 1 mgm of metal and the other containing, in addition to the metal, 2 gm of a uranyl sulfate which had been previously analyzed for fluoride. The fluoride was quantitatively recovered in the presence of beryllium, thorium, and iron. It was found that the addition of 0.5 gm of sulfate ion aided in obtaining complete recovery of the fluoride when 1 mgm of zirconium was present. Recovery was low when the distillation was made from aluminum. Table III shows this data.

TABLE III

DISTILLATION OF FLUORIDE IN PRESENCE OF ONE MILLIGRAM OF SELECTED METALS

(Fluoride Complexing Agents)

Metal Present	UO_2SO_4 (gm)	F^- Present (μ gm)	F^- Recovered (μ gm)	Deviation (μ gm)
Aluminum	2	36	18	-18
	0	30	19	-11
	0	20	18	-2
Beryllium	2	36	37, 30	+1, -6
	0	30	30	0
Iron	2	36	27	-9
	0	30	26	-4
Thorium	2	36	34	-2
	0	30	22	-8
Zirconium	2	36	31	-5
	0	30	3, 1	-27, -29
	0*	30	28	-2

*0.5 gm sulfate added

F. SEPARATION OF BERYLLIUM BY ION EXCHANGE

Ion exchange was investigated as a means of removing large amounts of metal ions, uranium in particular, from microgram-quantities of beryllium. The anionic resin IRA-400 in the sulfate form removes the negatively charged uranyl sulfate complex[13] and the beryllium will pass through the resin (at pH 1.5). Using this technique, 1 to 2 gm of uranyl sulfate can be separated from microgram-amounts of beryllium; however, some interference is picked up from the resin itself which results in an increase in absorbance. (This could be a small amount of an amine from resin break down, but no work was conducted to determine the exact cause.) For this reason, the eluate containing the beryllium was first fumed to near dryness with 0.5 mℓ of perchloric acid in order to destroy any organic matter, then the beryllium color was developed in the usual manner. However, the beryllium recovery was consistently low when the ion exchange—perchloric acid fuming method was used. Therefore, when this procedure is to be followed, a standard curve must be prepared using these same conditions. The comparison of non-evaporation, evaporation with perchloric acid, and ion exchange followed by perchloric acid evaporation is shown in Fig. 3.

In order to investigate the low beryllium recovery obtained, evaporations were made in glass, quartz, and platinum, and the losses were similar for each type of vessel. Other workers have encountered this type of loss, and it is believed that the losses are not due to volatilization of the beryllium, but canbe attributed to the partial conversion of the beryllium to a relatively insoluble form.[14]

Since the results obtained by ion exchange—evaporation technique are reproducible, although low, the method can be applied if the standard curve is prepared in the same way.

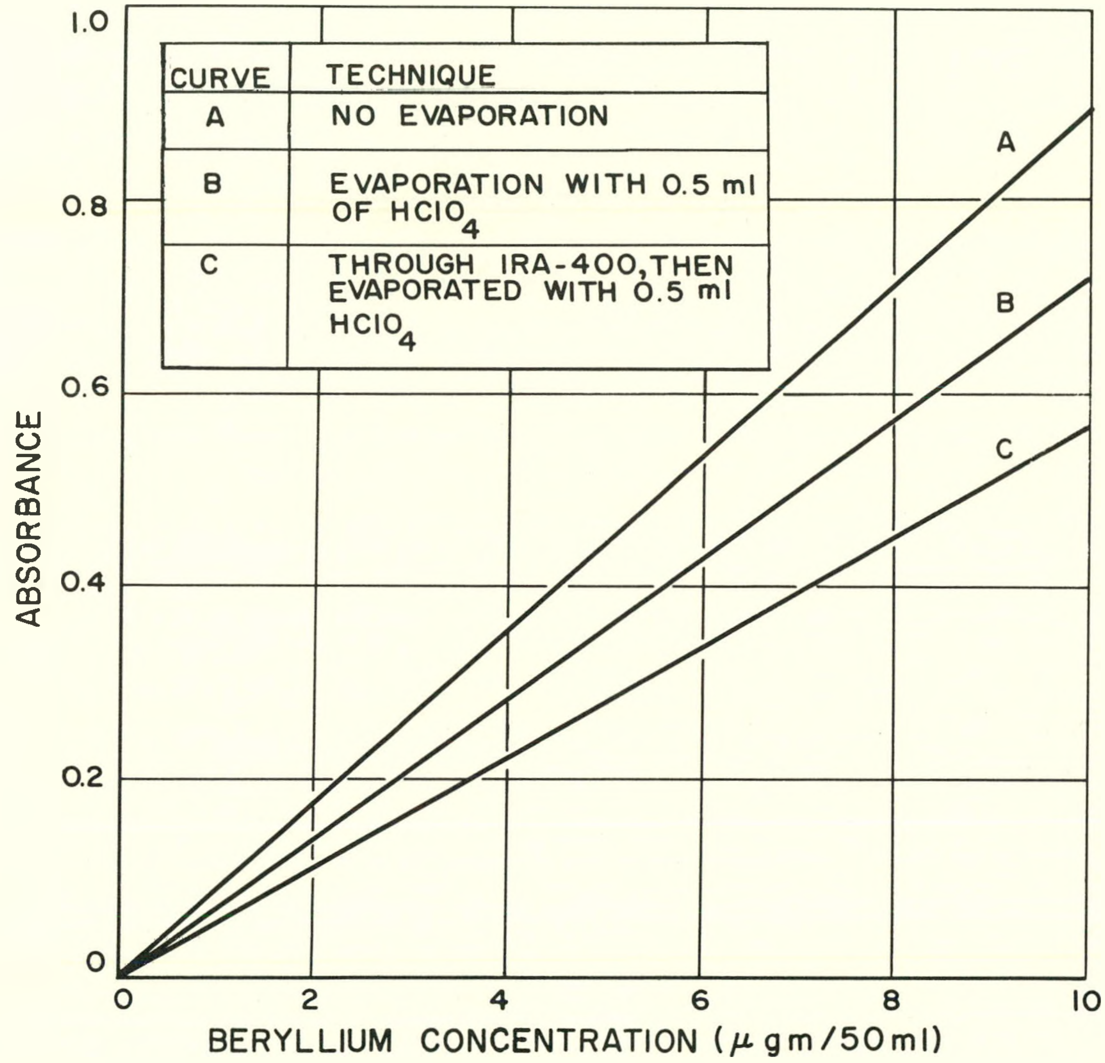

Fig. 3. Effect of $HClO_4$ Evaporation and Ion Exchange Technique

V. DISCUSSION

Data tabulated in Table IV show the deviation of a group of synthetic samples which were analyzed for beryllium by the Chrome Azurol S method. The method is accurate to ± 0.2 μ gm of beryllium per 50 mℓ volume.

TABLE IV

RECOVERY OF KNOWN QUANTITIES OF BERYLLIUM

Beryllium Added (μgm)	Beryllium Recovered (μgm)
1.0	0.9, 0.8, 0.8, 0.8, 0.8
5.0	5.2, 5.0, 5.0, 5.0, 4.9, 4.8, 4.8
10.0	10.2, 10.1, 10.1, 10.0, 9.9, 9.9

Beryllium determinations on the residues from ashed graphite samples are given in Table V. These samples were being examined for boron, strontium, calcium, magnesium, iron, and other elements as well as for beryllium. The limits of the method as outlined in the beryllium procedure are from 0.2 to 10 μ gm of beryllium per 50 mℓ volume; however, the procedure can be changed by reducing or increasing the volume and reagents to include lower or higher ranges.

TABLE V

DETERMINATION OF BERYLLIUM IN GRAPHITE ASH SAMPLES

Sample	Beryllium Found (μ gm/gm)
A	0.3, 0
B	2.0, 1.4
C	1.7, 1.4
D	1.3, 1.0
E	0.5, 0
F	1.0, 0.8, 0.6

Table VI shows the data obtained from the fluoride determination of several uranyl sulfate samples which had been produced commercially from the hexafluoride salt. The samples were first distilled from perchloric acid and the fluoride in the distillate was then determined by the beryllium—Chrome Azurol S method. The duplicates are in satisfactory agreement and the fluoride content of the commercial uranyl sulfate was shown to be sufficiently low. Consideration should also be given to the impurities listed in Table III.

TABLE VI

ANALYSIS OF URANYL SULFATE SAMPLES BY THE DISTILLATION METHOD

Sample	Sample Weight (gm)	Fluoride Concentration (μ gm/gm)
A	1.0	0, 0
B	1.0	12
	2.0	12
C	2.0	3, 3, 3, 2, 1
D	1.0	0
	1.5	4
E	1.0	9, 8
	1.5	5
F	1.0	6
	1.5	8
G	1.0	9
	1.5	6

The beryllium—Chrome Azurol S method for fluoride has the advantage of being more sensitive than other methods tried in this laboratory. The method is easily reproducible to ± 1 μgm of fluoride per 50 mℓ volume. The sensitivity would be increased if smaller volumes were used.

The interfering ions mentioned for beryllium and fluoride must be removed or accounted for in the standard curve preparation.

VI. CONCLUSIONS

Beryllium can be determined by the Chrome Azurol S method with an accuracy of ± 0.2 μgm beryllium per 50 mℓ volume. Large amounts of uranium, which interfere, can be removed by an ion exchange technique, and the effect of small quantities of iron and uranium can be obviated by the addition of hydroxylamine hydrochloride solution. This method should be useful for the direct determination of beryllium in air and in dust samples.

The use of the beryllium—Chrome Azurol S complex for the determination of fluoride is reproducible to ± 1 μgm fluoride per 50 mℓ volume. Interferences can be removed by prior distillation or pyrohydrolysis. The method has been successfully applied to the determination of fluoride in uranyl sulfate samples.

The advantages of using the Chrome Azurol S methods described for beryllium and fluoride are:

1) The reproducibility from day to day.
2) The stability of the colored complex.
3) The use of pyridine—hydrochloric acid buffer which assures rigid pH control and enhances the sensitivity of the method.
4) The simple and rapid technique involved.

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