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**SOME PROPERTIES OF SULFOACETIC ACID
AND 3-SULFOPROPIONIC ACID AND THEIR
USE AS ANALYTICAL MASKING AGENTS**

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SOME PROPERTIES OF SULFOACETIC ACID AND 3-SULFOPROPIONIC
ACID AND THEIR USE AS ANALYTICAL MASKING AGENTS*

by

Joseph Zimmerman and C. V. Banks

ABSTRACT

The values of K_{a2} for sulfoacetic and 3-sulfopropionic acids were determined potentiometrically. The values are $(8.6 \pm 0.3) \times 10^{-5}$ and $(3.0 \pm 0.1) \times 10^{-5}$, respectively. These values of K_{a2} were much lower than those predicted by the Branch and Calvin equation for the calculation of values of pK_a of derivatives of acetic acid.

The presence of intramolecular hydrogen bonds in sulfoacetate and 3-sulfopropionate accounted for some of the discrepancy between the calculated and observed values of K_{a2} for sulfoacetate and 3-sulfopropionate.

A proposition was made that the assumption of single bond character for the sulfur-oxygen bond in the Branch and Calvin treatment yields high results for the values of K_{a2} of acids with substituted sulfonate groups. It was suggested that the sulfonate group be classified as a resonating group for the Branch and Calvin treatment, and that it be given an inductive constant as a unit.

The water solubility of acetate at pH 5.0 was found to be much greater than sulfoacetate or 3-sulfopropionate at this pH.

At any given concentration, acetate was found to be a more effective masking agent for thorium than either sulfoacetate or 3-sulfopropionate. The three masking agents in the order of their decreasing masking efficiencies are, acetate > 3-sulfopropionate > sulfoacetate.

A method for the determination of trace amounts of aluminum in thorium was developed using Enta and 3-sulfopropionate to mask the thorium. Aluminum was extracted from aqueous thorium solutions with a 0.5 per cent solution of 8-quinolinol in chloroform. The aluminum was determined spectrophotometrically as the tris(8-quinolinolo)aluminum(III) complex.

* This report is based on an M.S. thesis by Joseph Zimmerman submitted June, 1956, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

INTRODUCTION

The preparation of highly pure thorium metal has introduced the necessity of developing accurate methods for the determination of trace metallic impurities, e.g., aluminum, in this pure metal. The spectrophotometric determination of trace quantities of aluminum in various substances, following a chloroform-8-quinolinol extraction has been utilized by many investigators (1, 11, 15, 17, 21, 23, 25, 35, 36, 40). Only Margerum, Sprain and Banks (21) have applied this procedure to the separation of aluminum from thorium. They found that a concentrated ammonium acetate solution at pH 5.0 could be used to mask thorium while aluminum was extracted. The ammonium acetate stabilized the pH of the aqueous solution, prevented the precipitation of thorium, prevented the extraction of thorium into the organic phase and permitted the quantitative extraction of aluminum into the organic phase. It was observed, however, that a small quantity of acetic acid was extracted into the chloroform layer and subsequently caused a partial ionization of the 8-quinolinol. This produced, in turn, a color which interfered with the spectrophotometric determination of aluminum.

It is known that the addition of a sulfonate group to an organic molecule increases its water solubility. Sulfoacetic acid and 3-sulfopropionic acid were prepared and studied in an effort to obtain masking agents for thorium which were not extractable into chloroform.

Sulfoacetic acid has been prepared by the action of sulfuric acid (22), chlorosulfonic acid (6), and sulfur trioxide (39) upon acetic acid; hydrogen peroxide (31) and silver sulfate (28) upon dithiodiacetic acid; nitric acid upon mercaptoacetic acid (9); silver sulfate upon acetyl chloride (16); sulfuric acid upon acetic anhydride (12); and chromic acid upon 2-hydroxyethanesulfonic acid (10). The methods most often employed for the preparation of sulfoacetic acid are those of Strecker (38) and Stillich (37). Chloroacetic acid is reacted with sodium or potassium sulfite in basic solution. The barium salt of sulfoacetic acid can be obtained by adding an excess of barium chloride to the reaction mixture.

Backer (2) obtained a value of 8.9×10^{-5} for the K_{a2}' of sulfoacetic acid by measuring the conductivity of solutions of the acid, its monosodium salt and its disodium salt. Backer (3) subsequently obtained values for K_{a2}' of 7.2 and 9.7×10^{-5} by measuring the pH of solutions of the monosodium salt and of equal mixtures of the monosodium and disodium salts. The three values of K_{a2}' were obtained by averaging results of each group of measurements, each taken over a wide range of concentrations.

3-Sulfopropionic acid has been prepared by the action of ammonium sulfite upon 3-iodopropionic acid (7,29), silver sulfate upon 3,3'-dithiodipropionic acid (28) and ammonium bisulfite upon acrylic acid (30). Backer (4) prepared 3-sulfopropionic acid by catalytic hydrogenation of ammonium 3-sulfoacrylate.

He obtained the latter either by the reaction between ammonium propionate and ammonium bisulfite or by the reaction between ammonium 3-chloroacrylate and ammonium sulfite. Kharasch (18) obtained the inner anhydride of 3-sulfopropionic acid by reacting propionic acid with sulfuryl chloride. The solid anhydride obtained can be readily converted to the acid by hydrolysis.

EXPERIMENTAL WORK

Apparatus

Spectrophotometers

A Beckman Model DU quartz spectrophotometer and Cary Model 12 recording spectrophotometer were used to measure absorbances.

A Baird Model B recording infrared spectrophotometer and a Perkin-Elmer Model 13 recording infrared spectrophotometer were used to obtain infrared spectra.

pH meter

A Beckman Model G pH meter was used for all potentiometric titrations and pH measurements.

Materials and Reagents

1. Absolute Ethyl Alcohol. Technical.
2. Aluminum Solution. A stock solution of aluminum chloride was prepared from very pure aluminum metal, kindly supplied by J. R. Churchill of the Aluminum Company of America.
3. Aniline. J. T. Baker Chemical Co. Redistilled.
4. Barium Chloride. Reagent grade.
5. Chloroacetic Acid. Matheson, Coleman and Bell.
6. Chloroform. Reagent grade. Purified by extracting with a solution two molar in ammonium hydroxide and ammonium chloride and then distilling. Stabilized by the addition of one per cent, by volume, of absolute ethyl alcohol.
7. Disodium salt of N,N,N',N'-Tetrakis-(carboxymethyl)-ethylenediamine. Geigy Chemical Co. A 0.058 molar solution was purified by extracting with a 10 per cent solution of 8-quinolinol in chloroform and then by extracting with chloroform.

8. Disodium salt of N,N,N',N'-Tetrakis-(carboxymethyl)-1,2-cyclohexane-diamine. Hach Chemical Co. A 0.056 molar solution was purified by extracting with a 10 per cent solution of 8-quinolinol in chloroform and then by extracting with chloroform.
9. Hydrochloric Acid. C.P. Concentrated acid of sp. gr. 1.19.
10. Hydroxylammonium Chloride. A 10 per cent aqueous solution was prepared from reagent-grade hydroxylammonium chloride.
11. Methyl Alcohol. Technical.
12. Petroleum Ether. Boiling range 30 - 60°.
13. 1,10-Phenanthroline. A 0.1 per cent aqueous solution was prepared from reagent-grade 1,10-phenanthroline 1-hydrate. G. Frederick Smith Chemical Co.
14. Propionic Acid. Fisher certified reagent.
15. 8-Quinolinol. A 0.5 per cent solution was prepared by dissolving reagent-grade 8-quinolinol (J. T. Baker Chemical Co.) in purified chloroform.
16. Sodium Carbonate. Reagent grade. Anhydrous.
17. Sodium Hydroxide. Reagent grade.
18. Sodium Sulfate. Reagent grade. Anhydrous.
19. Sodium Sulfite. Reagent grade. Anhydrous.
20. Sulfoacetic Acid. Technical. City Chemical Co., New York.
21. Sulfuric Acid. C.P. Concentrated acid of sp. gr. 1.84.
22. Sulfuryl Chloride. Purified. J. T. Baker Chemical Co.
23. Thionyl Chloride. Purified. J. T. Baker Chemical Co.
24. Thorium Nitrate. A 0.11 molar stock solution was prepared from especially purified thorium nitrate 4-hydrate.

Preparation of Sulfoacetic Acid

Barium sulfoacetate was prepared by the method of Stillich (37). A water solution of chloroacetic acid was neutralized with sodium hydroxide. Sodium sulfite was then added and the solution was heated at about

98° for one hour. An excess of barium chloride was added to the reaction mixture and the resulting insoluble barium sulfoacetate was filtered. A suspension of the barium salt in water was boiled for about an hour to remove water-soluble impurities. The suspension was filtered to isolate the barium salt. Samples of the barium salt were suspended in water and shaken with cation exchange resin (Dowex 50 - X12) which was in the hydrogen cycle. Some of the barium sulfoacetate was converted to sulfoacetic acid in this way. Small quantities of sulfurous acid which were found in the exchanged acid solution were removed by heating the solutions on a steam bath. Potentiometric titrations of the acid solutions indicated the presence of a fairly pure dibasic acid. The utilization of the cation exchange resin was eliminated, however, because sulfoacetic acid could be prepared by this process only in small quantities and the exchange was not very efficient. The barium sulfoacetate was reacted with an excess of sulfuric acid. The barium sulfate was filtered and the filtrate was heated to remove sulfurous acid. A sample of the filtrate was then titrated potentiometrically in order to determine the quantity of excess sulfuric acid present. An equivalent quantity of barium hydroxide was added to the filtrate to precipitate the excess sulfuric acid. The barium sulfate was filtered and the resulting filtrate was titrated potentiometrically. The titration indicated the presence of a fairly pure dibasic acid.

Attempts to isolate the sulfoacetic acid in solid form by evaporation of the acid solution under vacuum and by azeotropic distillation of the solution with benzene were unsuccessful. No solid product was obtained. The disodium salt of sulfoacetic acid was isolated by neutralizing an acid solution to pH 9 with sodium hydroxide, concentrating the solution on a steam bath and adding a 3:1 solution of ethanol and methanol. The white product was filtered and dried at 110° in an oven. A sample of the salt was dissolved in water and titrated potentiometrically with standard hydrochloric acid and its equivalent weight was found to be 190. The equivalent weight of pure disodium sulfoacetate is 184. The salt was analyzed for sulfur by the method of Fritz and Yamamura (14). This method involves the combustion of a sample containing sulfur in a Paar bomb, the neutralization of the combusted sample to pH 3 with hydrochloric acid, the elimination of interfering anions and cations utilizing first an alumina column and then a cation exchange column, and finally the titration of the sulfate ion with barium perchlorate in 80 per cent ethanol with thorin used as internal indicator. The calculated sulfur content of disodium sulfoacetate is 17.4 per cent and the sulfur content of the sample was found to be 17.6 per cent.

After the work reported above had been completed, technical-grade sulfoacetic acid was made available commercially by the City Chemical Company of New York. Some sulfoacetic acid was obtained from this source. It was found to be chunky and discolored, but potentiometric titrations indicated that solutions of the product had no significant quantity of acid impurity.

A 3.0 molar solution of the sulfoacetic acid obtained from the City Chemical Company was purified by adjusting its pH to 10, adding decolorizing

charcoal and filtering. The solution was then extracted with a 10 per cent solution of 8-quinolinol in chloroform. It was then extracted with chloroform alone. The solution was then converted to the acid form by passing it through a cation exchange column.

Preparation of 3-Sulfopropionic Acid

The inner anhydride of 3-sulfopropionic acid was prepared by the method of Kharasch (18). Propionic acid was reacted with sulfuryl chloride for 5 to 7 hours under the influence of a 200-watt incandescent light. A temperature of 50° to 60° was maintained. Sulfur dioxide and hydrochloric acid were partially removed under vacuum, and the inner anhydride of 3-sulfopropionic acid was precipitated by the addition of petroleum ether. The white sticky product was recrystallized from thionyl chloride. The product was then further purified by refluxing it with several portions of petroleum ether. It was then dried in a vacuum desiccator over phosphorus pentoxide. The crystalline anhydride was found to be highly hygroscopic. It was readily converted to 3-sulfopropionic acid by allowing it to stand in air or by dissolving it in water. The acid itself was also found to be quite hygroscopic.

Samples of the anhydride were titrated with standard sodium hydroxide. The titrations indicated the presence of a very pure dibasic acid. The equivalent weight of the samples varied from 68.3 to 69.4. The equivalent weight of the anhydride is 68.0. The samples of the anhydride were analyzed for sulfur using the method of Fritz and Yamamura (14). The results are shown in Table 1. The theoretical sulfur content of these samples was calculated from their equivalent weights. The latter values indicate the extent to which the anhydride samples had absorbed water.

The disodium salt of 3-sulfopropionic acid was prepared by neutralizing a water solution of the anhydride to pH 9 with sodium hydroxide, concentrating the solution on a steam bath and precipitating with a 3:1 solution of ethanol and methanol. The salt was dried in an oven at 110° and samples of it were titrated potentiometrically with hydrochloric acid. Equivalent weights of 203 and 201 were found for the disodium salt. The equivalent weight of disodium 3-sulfopropionate is 198. Samples of the disodium salt were analyzed for sulfur. The results are shown in Table 1.

The anilinium salt of 3-sulfopropionanilide was prepared by reacting the anhydride with redistilled aniline. The product was recrystallized from warm water. A sample of the anilinium salt was dissolved in water and titrated with standard sodium hydroxide. Its equivalent weight was found to be 321. The equivalent weight of the anilinium salt of 3-sulfopropionanilide is 322. The sample was analyzed for sulfur. The result is shown in Table 1.

Table 1
Results of sulfur analyses

Compound	Equivalent wt.	% S calc.	% S found
Anhydride	68.6	23.4	23.2
Anhydride	69.5	23.1	22.9
Anhydride	69.1	23.2	23.2
Anhydride	69.2	23.2	23.3
Anhydride	68.5	23.4	23.5
Anhydride	68.8	23.3	23.5
Anhydride	68.6	23.4	23.5
Anhydride	69.4	23.1	23.2
Disodium salt	203	16.2	16.4
Disodium salt	201	16.2	16.0
Anilinium salt	322	9.94	9.95

The Values of K_{a2} for Sulfoacetic Acid
and 3-Sulfopropionic Acid

Potentiometric titrations of solutions of sulfoacetic and 3-sulfopropionic acid indicated that both acids had greater ionization constants than acetic acid. The value for pK_{a2} of sulfoacetic acid was observed to lie between 3.70 and 3.90 while that of 3-sulfopropionic acid was observed to lie between 4.20 and 4.30.

Calculation of values of pK_{a2}

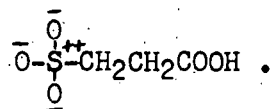
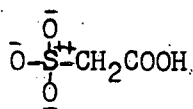
The approximate pK_{a2} values of sulfoacetic and 3-sulfopropionic acids were calculated of values of pK_a for derivatives of acetic acid (8, p. 221). This empirical equation gives a value for the pK_a of acetic acid derivatives, which is based upon the inductive effect of substituent groups. The structure of the

acid is drawn with all formal charges (if any) placed upon particular atoms of the substituted group or groups. From the inductive effect of each atom, the inductive effect of the formal charge on each atom, and the effect of the position of the atom with respect to the alpha carbon atom, the pKa can be calculated as follows:

$$\log K = -4.75 + \frac{A\alpha \sum I_{\alpha} i_{\alpha}}{1 + |B\alpha \sum I_{\alpha} i_{\alpha}|} + \log \frac{n'}{m'}$$

In the formula, n' and m' are the numbers of equivalent carboxy and carboxylate groups in the acid and its ion, respectively. $A\alpha$ and $B\alpha$ are constants for derivatives of acetic acid. I_{α} is the inductive constant of a particular atom and of its charge. α is the fraction which reduces the inductive effect for each transmission across an atom and i_{α} is the number of atoms intervening between a substituent group and the alpha carbon atom. Hydrogen atoms are given no inductive constant.

Branch and Calvin assumed that sulfur-oxygen bonds were single bonds. They stated that in the sulfonate group the sulfur atom has a formal positive charge of two and each oxygen atom has a formal negative charge of one. Therefore, the formal structures drawn for sulfoacetate and 3-sulfopropionate were the following:



The inductive constants for sulfur, oxygen and carbon are given as 3.4, 4.0 and -0.4, respectively. The inductive constant for each formal charge is given as ± 12.3 , α is equal to $1/2.8$ and $A\alpha$ and $B\alpha$ are given as 0.3 and 0.03, respectively. The pKa₂ values for sulfoacetate and 3-sulfopropionate were calculated as follows:

Sulfoacetate,

$$\log K = -4.75 +$$

$$\frac{0.3 \left[3.4 + \frac{(3)(4)}{2.8} + (2)(12.3) - \frac{(3)(12.3)}{2.8} \right]}{1 + 0.03 \left[3.4 + \frac{(3)(4)}{2.8} + (2)(12.3) - \frac{(3)(12.3)}{2.8} \right]}$$

from which $\log K = -1.12$ and $K = 7.6 \times 10^{-2}$.

3-Sulfopropionate,

$$\log K = -4.75 +$$

$$\frac{0.3 \left[-0.4 + \frac{3.4}{2.8} + \frac{(3)(4)}{(2.8)^2} + \frac{(2)(12.3)}{2.8} - \frac{(3)(12.3)}{(2.8)^2} \right]}{1 + 0.03 \left[-0.4 + \frac{3.4}{2.8} + \frac{(3)(4)}{(2.8)^2} + \frac{(2)(12.3)}{2.8} - \frac{(3)(12.3)}{(2.8)^2} \right]},$$

from which $\log K = -3.14$ and $K = 7.25 \times 10^{-4}$.

The Branch and Calvin equation therefore predicts that the dissociation of acetic acid and propionic acid should be enhanced by the addition of the sulfonate group. The calculated values of K_{a2} were much higher than the observed values of K_{a2}' for the two acids, but other effects probably tend to lower the dissociation.

Determination of the thermodynamic values of K_{a2}

It was found that ultraviolet spectrophotometry could not conveniently be utilized to determine the thermodynamic values of K_{a2} for sulfoacetic and 3-sulfopropionic acids. The absorption band for each acid was found to occur between 205 and 215 millimicrons. In this region, carbon dioxide interferes very significantly with all spectra.

The values of K_{a2} for sulfoacetic and 3-sulfopropionic acids were determined potentiometrically. Solutions of varied concentrations of the two acids were titrated with standard, carbonate-free sodium hydroxide under a stream of nitrogen gas. For each titration, the pH at the point midway between the first and second breaks (pK_{a2}') was plotted against the square root of the ionic strength, $\sqrt{\mu}$. For these acids, the ionic strength at the point midway between the first and second breaks was found to be equal to twice the molar concentration. These data are shown in Table 2. The thermodynamic values of pK_{a2} for sulfoacetic and 3-sulfopropionic acids were obtained by extrapolating the two straight lines to zero ionic strength as shown in Figure 1. The value for sulfoacetic acid was found to be 4.065 ± 0.015 and that for 3-sulfopropionic acid was found to be 4.525 ± 0.015 . These values correspond to K_{a2} values of $(8.6 \pm 0.3) \times 10^{-5}$ and $(3.0 \pm 0.1) \times 10^{-5}$, respectively. The ratios of the calculated to the experimental value of K_{a2} for sulfoacetic acid and 3-sulfopropionic acid were 885/1 and 24/1, respectively. The difference in ratio indicated that some factor was lowering the dissociation constant of sulfoacetic acid to a much greater extent than that of 3-sulfopropionic acid.

Table 2

Potentiometric titration data for sulfoacetic acid
and 3-sulfopropionic acid

Acid	Molar concentration	\sqrt{c}	Number of titrations	Average pK_{a2}
Sulfoacetic	0.131	0.513	4	3.69
Sulfoacetic	0.0937	0.445	4	3.73
Sulfoacetic	0.0600	0.347	4	3.79
Sulfoacetic	0.0564	0.336	2	3.81
Sulfoacetic	0.0348	0.264	3	3.84
Sulfoacetic	0.0264	0.230	2	3.89
Sulfoacetic	0.0244	0.221	3	3.89
Sulfoacetic	0.0145	0.171	2	3.94
Sulfoacetic	0.0084	0.130	2	3.97
Sulfoacetic	0.0079	0.125	3	3.97
3-Sulfopropionic	0.0485	0.312	3	4.33
3-Sulfopropionic	0.0286	0.240	3	4.38
3-Sulfopropionic	0.0154	0.172	3	4.42
3-Sulfopropionic	0.0090	0.135	3	4.44
3-Sulfopropionic	0.0060	0.108	3	4.47

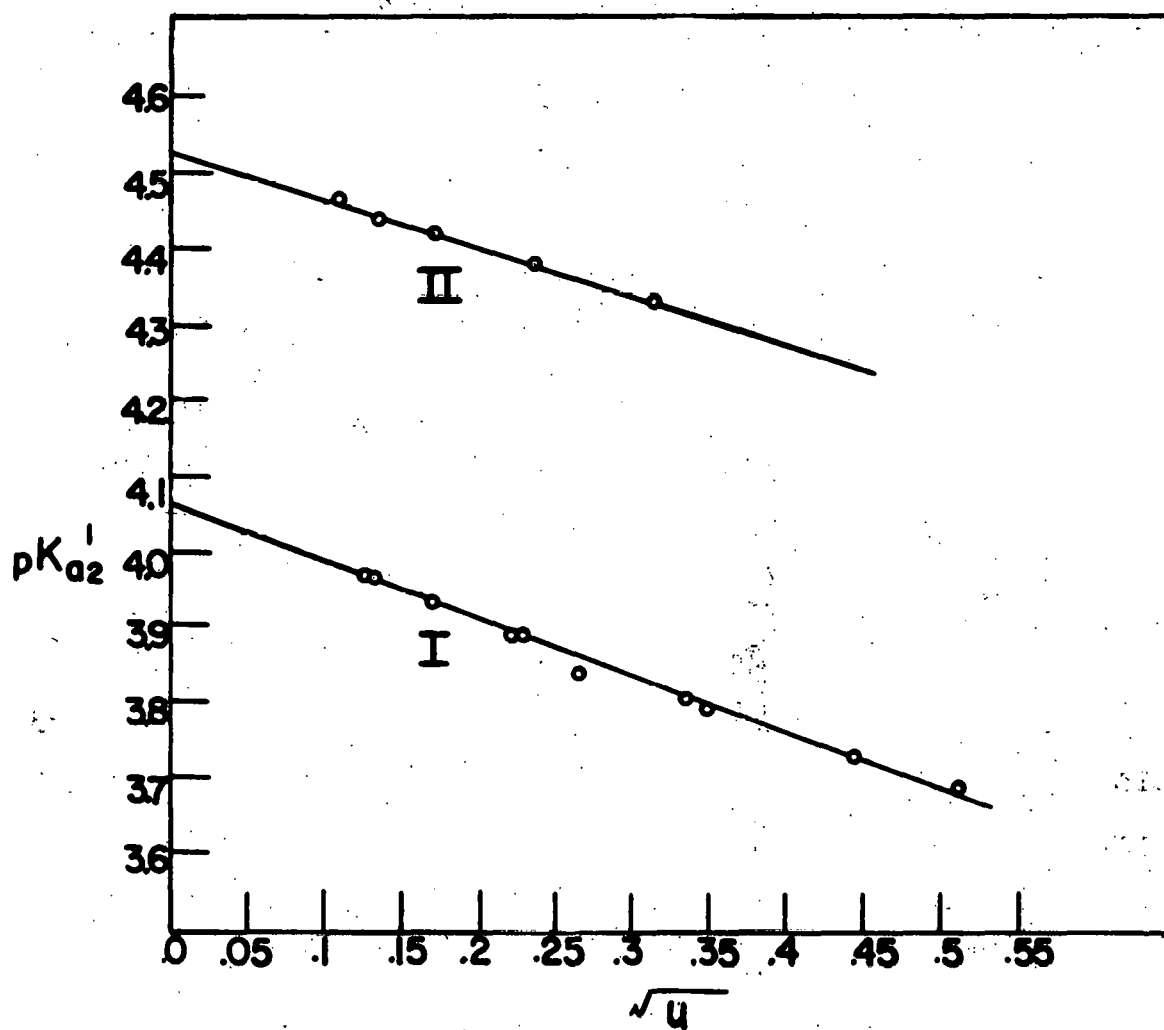


Figure 1. Variation of pK_{a2}' with the square root of the ionic strength for I, sulfoacetic acid and II, 3-sulfopropionic acid.

Evidence for Hydrogen Bonding

Models of the sulfoacetic acid and 3-sulfopropionic acid molecules were assembled and it was observed that the formation of intramolecular hydrogen bonding was possible in both molecules. On this basis it was decided that the infrared spectra of the compounds should be observed.

A solution of an approximately equivalent mixture of the monosodium and disodium salts of sulfoacetic acid was prepared by adjusting the pH of a 3.0 molar solution of the acid to 2.30. A solution of an approximately equivalent mixture of the monosodium and disodium salts of 3-sulfopropionic acid was prepared by adjusting the pH of a 1.5 molar solution of the acid to 3.37. Each solution was evaporated to dryness on a steam bath. A sample of each solid product was ground to a powder and dried in an Abderhalden drying apparatus under vacuum, over phosphorus pentoxide with heat provided by toluene reflux. The samples were then reground, and were dried in the same manner with heat provided by glacial acetic acid reflux. The infrared spectra of samples of the two powders were obtained with a Baird recording infrared spectrophotometer using Nujol mull as solvent and sodium chloride cells. An infrared spectrum was also obtained for a slightly wet sulfoacetate sample. The spectra, which are shown in Figure 2, indicate the presence of intramolecular hydrogen bonding in both of the dry samples. The sharp absorption band in the spectrum of 3-sulfopropionate at 2.98 microns is probably due to either the presence of water or to the formation of intermolecular hydrogen bonds. The sharp absorption band at 3.2 microns is probably due to the formation of intramolecular hydrogen bonds. The sulfoacetate spectrum shows a slight absorption band at 2.98 microns which might be caused either by the presence of a trace amount of water or by the formation of intermolecular hydrogen bonds. The shoulder at about 3.2 microns on the band of the Nujol mull, probably represents the beginning of a band which is caused by intramolecular hydrogen bonding. The fact that the band of the Nujol mull partially masks the absorption band at about 3.2 microns for sulfoacetate, means that the latter occurs at a higher wave length and therefore represents stronger intramolecular hydrogen bonding than is present in 3-sulfopropionate. The spectrum of the wet sulfoacetate sample shows a wide absorption band which has a maximum at about 2.96 microns and which extends to about 3.2 microns and masks the bands characteristic of sulfoacetate.

Spectra of the powders of sulfoacetate and 3-sulfopropionate were obtained with a Perkin-Elmer recording infrared spectrophotometer using the KBr pellet technique. The spectra obtained also indicated that the intramolecular hydrogen bond for sulfoacetate occurred at a higher wave length than that of 3-sulfopropionate.

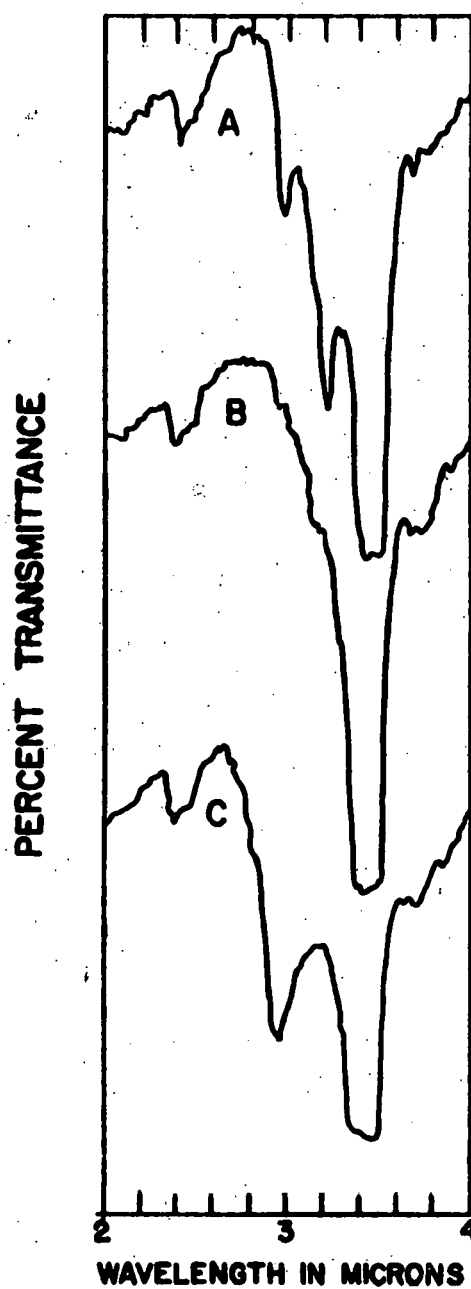


Figure 2. Infrared absorption spectra of A, 3-sulfopropionate, B, sulfoacetate and C, wet sulfoacetate.

Sulfoacetic Acid and 3-Sulfopropionic Acid
as Masking Agents for Thorium

Solubility of sulfoacetate and 3-sulfopropionate at pH 5.0

Margerum, Sprain and Banks (21) were able to utilize an 18 molar solution of acetate to mask thorium. The disodium salts of sulfoacetic acid and 3-sulfopropionic acid were dissolved in water and it was found that at a pH of 5.0 the maximum solubility of these salts were approximately 3.0 molar and 2.0 molar, respectively. The high molecular weight of the salts (184 and 198, respectively) compared to the molecular weight of sodium acetate (81), may account for the difference in water solubility.

Margerum, Sprain and Banks (21) found that when a 1 molar solution of acetate at pH 5.0 was equilibrated with a 1 per cent solution of 8-quinolinol in chloroform, some acetic acid was taken into the chloroform phase. This small amount of acetic acid effected partial ionization of the 8-quinolinol and a strong absorption band at 372 millimicrons was observed in the spectrum of the equilibrated chloroform-8-quinolinol solution.

Solutions of 3.0 molar sulfoacetate and 2.0 molar 3-sulfopropionate were adjusted to pH 5.0. Both solutions were scrubbed with a concentrated solution of 8-quinolinol in chloroform and then with chloroform alone. Each scrubbed solution was equilibrated with a solution of 1 per cent 8-quinolinol in chloroform. The spectra of the chloroform-8-quinolinol solutions were not affected by the equilibrations. It was concluded that neither sulfoacetic acid nor sulfopropionic acid was taken into the chloroform phase.

The ability of sulfoacetate and 3-sulfopropionate to
prevent the precipitation of thorium as thorium
hydroxide from aqueous solutions

By using a 3.0 molar solution of sulfoacetate, a 2.0 molar solution of 3-sulfopropionate and a 0.043 molar solution of thorium nitrate 4-hydrate, the ability of each masking agent to prevent the precipitation of thorium as thorium hydroxide was studied. Solutions were prepared in which the molar ratio of the masking agent to thorium was 50/1 and the pH of these solutions was varied. Solutions were also prepared in which the molar ratio was 10/1 and the pH of these solutions was varied. It was found that each masking agent was able to prevent the precipitation of thorium up to a pH of 5.5 when the molar ratio of masking agent to thorium was 50/1. When the molar ratio was 10/1, each masking agent was able to prevent the precipitation of thorium up to a pH of 4.9.

The ability of sulfoacetate and 3-sulfopropionate to prevent the extraction of thorium from aqueous solutions at pH 5.0 with 8-quinolinol in chloroform.

By using a 3.0 molar solution of sulfoacetate, a 2.0 molar solution of 3-sulfopropionate, a 0.043 molar solution of thorium nitrate 4-hydrate and solutions of chloroform-8-quinolinol, the ability of each masking agent to prevent the extraction of thorium into the chloroform-8-quinolinol solution was studied. Solutions were prepared in which the molar ratio of masking agent to thorium was varied, and the pH of each solution was adjusted to 5.0. The solutions were extracted with 1.0, 0.5 and 0.2 per cent solutions of 8-quinolinol in chloroform.

When extraction was performed with a 1 per cent chloroform-8-quinolinol solution, neither sulfoacetate nor 3-sulfopropionate prevented the extraction of thorium into the chloroform phase even when the molar ratio of masking agent to thorium was as high as 1500/1. When extraction was performed with a 0.5 per cent solution of chloroform-8-quinolinol, sulfoacetate did not prevent the extraction of thorium into the chloroform phase even when the molar ratio was as high as 1500/1. 3-Sulfopropionate prevented the extraction of thorium at molar ratios greater than 500/1. When a 0.2 per cent solution of chloroform-8-quinolinol was used for the extractions, sulfoacetate and 3-sulfopropionate did prevent the extraction of thorium at molar ratios greater than 500/1 and 50/1, respectively. It was found that holding the molar ratio of sulfoacetate of 3-sulfopropionate to thorium constant while lowering the concentration of both masking agent and thorium, resulted in an increase in the extractability of thorium into the chloroform phase. During these studies, it was noted that solutions which contained sulfoacetate often highly dispersed emulsions.

The relative masking abilities of acetate, sulfoacetate, and 3-sulfopropionate at pH 5.0.

The results given in the preceding section indicated that 3-sulfopropionate is a more effective masking agent for thorium than is sulfoacetate. Studies similar to the ones made in the above section were carried out using solutions of 0.2 molar 3-sulfopropionate, 0.3 molar sulfoacetate, 0.2 molar acetate, 0.0043 molar thorium nitrate 4-hydrate and 0.1 and 0.15 per cent solutions of 8-quinolinol in chloroform. The abilities of the three masking agents to prevent the extraction of thorium into the chloroform-8-quinolinol phase were compared.

When extraction was performed with a 0.1 per cent chloroform-8-quinolinol solution, all three masking agents prevented the extraction of thorium, even when the molar ratio of masking agent to thorium was as low as 10/1. When extraction was performed with a 0.15 per cent chloroform-8-quinolinol solution, it was found that sulfoacetate did not prevent the extraction of thorium when the molar ratio was as high as 1500/1. 3-Sulfopropionate and acetate prevented

the extraction of thorium at molar ratios of 500/1 and 125/1, respectively. It was concluded that the three masking agents, in the order of their decreasing masking efficiencies, would be written as acetate > 3-sulfopropionate > sulfoacetate. This is also the order of their decreasing pK_{a2} values.

It was observed that a solution of 0.2 molar acetate did not prevent the extraction of thorium with a 0.25 per cent solution of 8-quinolinol in chloroform when the molar ratio of the acetate to thorium was 1000/1. Margerum, Sprain and Banks (21) were able to prevent the extraction of thorium into a 1 per cent solution of 8-quinolinol in chloroform when the molar ratio of acetate to thorium was 450/1 utilizing an 18 molar solution of acetate. The maximum concentration of sulfoacetate and 3-sulfopropionate in solution, however, can be no more than 3 molar and 2 molar, respectively. Furthermore, at any given concentration both sulfoacetate and 3-sulfopropionate are less efficient masking agents than is acetate. On these bases it was decided that a masking agent which could aid sulfoacetate and 3-sulfopropionate in the masking of thorium should be sought.

Use of N,N,N',N'-tetrakis-(carboxymethyl)-
ethylenediamine to aid sulfoacetate
and 3-sulfopropionate in the masking
of thorium

Hereinafter, N,N,N',N'-tetrakis-(carboxymethyl)-ethylenediamine will be referred to as Enta.

Sen Sarma and Mallik (33) utilized Enta as a masking agent for metals such as aluminum, thorium and iron in the precipitation of uranium with solutions of 8-quinolinol in chloroform. Claasen, Bastings and Visser (11) utilized Enta as a masking agent for many metals in the extraction of tris-(8-quinolinol) aluminum(III) with chloroform. In the latter case, an excess of Enta was added to a solution containing metal ions among which were trace amounts of aluminum. The solution was made alkaline and was required to stand for an hour in the presence of an alcohol solution of 8-quinolinol. The solution was then extracted with chloroform. Schwarzenbach (32, p.7) determined the formation constants of the thorium-Enta and aluminum-Enta complexes and found the values to be $10^{23.2}$ and $10^{16.1}$, respectively.

On the basis of the above findings, it was believed that Enta might be able to aid sulfoacetate and 3-sulfopropionate in the masking of thorium. A 0.056 molar solution of the disodium salt of Enta was adjusted to a pH of 5.0. The solution was scrubbed with a concentrated solution of 8-quinolinol in chloroform and then with chloroform alone. The scrubbed solution was equilibrated with a 1 per cent solution of 8-quinolinol in chloroform. The equilibration did not affect the spectra of the chloroform-8-quinolinol phase.

A thorium nitrate 4-hydrate solution was prepared so that approximately 0.2 gram of thorium would be present in 25 ml. of solution. The exact

equivalence of the Enta solution to the thorium solution was determined by the titration method of Fritz and Ford (13). Twenty-five-ml. portions of the thorium solution were titrated with Enta; Alizarin Red S was used as internal indicator. The pH of the solution of thorium was maintained between 2.5 and 3.0 throughout the titration. It was found that exactly 15.05 ml. of the Enta solution were required to titrate 25 ml. of the thorium solution. The thorium solution was calculated to be 0.034 molar and to contain 0.198 gram of thorium per 25 ml.

By using the 0.034 molar thorium solution, the 0.056 molar Enta solution and a 1.0 per cent solution of 8-quinolinol in chloroform, the ability of Enta to prevent the extraction of thorium into the chloroform-8-quinolinol solution was tested. To 25 ml. of the thorium solution, 16.5 ml. of Enta solution were added. The molar ratio of Enta to thorium was therefore 1.2/1 in this solution. The pH of the solution was adjusted to 5.0 and the solution was extracted with a 1.0 per cent solution of 8-quinolinol in chloroform. It was found that no thorium was extracted into the chloroform layer. It was also found, however, that microgram quantities of aluminum could not be extracted from aqueous solutions at pH 5.0, in which Enta was present in excess. Therefore, if Enta were used as an aid to sulfoacetate of 3-sulfopropionate, a quantity of it which would be less than equivalent to the quantity of thorium to be masked, should be added.

By using solutions of 0.056 molar Enta, 0.034 molar thorium, 3.0 molar sulfoacetate, 2.0 molar 3-sulfopropionate and 0.5 per cent 8-quinolinol in chloroform, the ability of a combination of Enta and either sulfoacetate or 3-sulfopropionate to prevent the extraction of thorium into the chloroform-8-quinolinol was studied.

To 20 ml. of thorium solution, 10 ml. of sulfoacetate solution were added. To this solution, 10 ml. of the Enta solution were then added and the pH was adjusted to 5.0. The solution was extracted with 10 ml. of 8-quinolinol solution. Thorium was not extracted into the chloroform phase. Both phases were allowed to remain in contact with each other and were reshaken every half hour. After about two hours thorium began to extract into the chloroform phase. The color of the chloroform phase darkened with each successive equilibration, indicating that more thorium was being extracted each time. After about 24 hours no further extraction of thorium was observed upon equilibration.

To 20 ml. of thorium solution, 10 ml. of Enta solution were added. To this solution, 10 ml. of sulfoacetate solution were then added and the pH was adjusted to 5.0. The solution was extracted with 10 ml. of 8-quinolinol solution. Some thorium was extracted into the chloroform phase. Both phases were allowed to remain in contact with each other and were reshaken every half hour. No further extraction of thorium was noted after the original equilibration.

To 20 ml. of thorium solution, 10 ml. of 3-sulfopropionate solution were added. To this solution, 10 ml. of Enta solution were added and the pH was

adjusted to 5.0. The solution was extracted with 10 ml. of sulfoacetate solution. A slight quantity of thorium was extracted into the chloroform phase. The two phases were allowed to remain in contact with each other and after only 3 minutes, further equilibration of the two phases resulted in the extraction of more thorium into the chloroform phase. The two phases were equilibrated every 15 minutes and the color of the chloroform phase darkened with each successive equilibration. After about 3 hours no further extraction of thorium was observed upon equilibration.

To 20 ml. of the thorium solution, 10 ml. of Enta solution were added. To this solution, 10 ml. of the 3-sulfopropionate solution were added and the pH was adjusted to 5.0. The solution was extracted with 10 ml. of 8-quinolinol solution. It was found that some thorium was extracted into the chloroform phase. Both phases were allowed to stand in contact with each other and were reshaken every 15 minutes. No further extraction of thorium was noted after the original equilibration.

It was therefore concluded that the order of addition of masking agents is critical. Although the complex formed between thorium and sulfoacetate is weaker than that formed between thorium and Enta, the former probably dissociates at a slow enough rate to permit Enta, if it is added last, to be present in excess of the thorium. The same supposition can be applied to 3-sulfopropionate. It was observed, however, that the system thorium-3-sulfopropionate-Enta approached equilibrium more rapidly than the system thorium-sulfoacetate-Enta. This observation was found to be puzzling since 3-sulfopropionate was found to be a more effective masking agent for thorium than was sulfoacetate. Difference in the kinetics of formation and dissociation of the thorium complexes of 3-sulfopropionate and sulfoacetate would probably explain the anomalous observations.

A solution of thorium nitrate 4-hydrate was prepared in which approximately 0.2 gram of thorium was present in 10 ml. of solution. This solution was titrated with 0.056 molar Enta. It was found that exactly 15.5 ml. of Enta solution were equivalent to 10 ml. of thorium solution. The thorium solution was therefore 0.087 molar and contained 0.202 gram of thorium in 10 ml. By using solutions of 0.087 molar thorium, 0.056 molar Enta, 3.0 molar sulfoacetate, 2.0 molar 3-sulfopropionate and 1.0 and 0.5 per cent 8-quinolinol in chloroform, the study of the masking ability of a combination of Enta and either sulfoacetate or 3-sulfopropionate was continued. To samples of 0.2 gram of thorium, 14 ml. of Enta solution were added. From 10 to 40 ml. of sulfoacetate solution or 3-sulfopropionate solution were added to these solutions. The pH of each solution was adjusted to 5.0. The solutions were extracted with 10 ml. of either a 1 per cent or a 0.5 per cent solution of 8-quinolinol in chloroform.

It was found that even with the aid of 14 ml. of Enta solution, neither sulfoacetate nor 3-sulfopropionate prevented the extraction of much thorium into the chloroform phase when a 1.0 per cent solution of 8-quinolinol in chloroform was employed for the extraction. It was found that 35 ml. of 3.0 molar

sulfoacetate solution or 25 ml. of 2.0 molar 3-sulfopropionate solution, with the aid of 14 ml. of Enta solution, almost completely prevented the extraction of thorium into the chloroform phase when a 0.5 per cent solution of 8-quinolinol in chloroform was employed for the extraction. When sulfoacetate was utilized, however, highly dispersed emulsions were formed which could not be broken down without utilization of a centrifuge.

It was decided that a method for the extraction and subsequent spectrophotometric determination of trace amounts of aluminum in thorium would be worked out utilizing Enta and 3-sulfopropionate as masking agents for thorium. Sulfoacetate was shown to be a less effective masking agent for thorium than 3-sulfopropionate. Moreover, highly dispersed emulsions which were difficult to break down were almost always formed when solutions containing sulfoacetate were extracted with chloroform-8-quinolinol solutions.

The Determination of Aluminum in Thorium

Aluminum extractions

A stock solution of aluminum chloride was prepared by dissolving very pure aluminum metal in concentrated hydrochloric acid. An aluminum solution which contained 10 micrograms of aluminum per ml. was prepared from the aluminum stock solution.

Solutions containing 40 micrograms of aluminum were buffered with 30 ml. of 2.0 molar 3-sulfopropionate solution. The solutions were extracted with 20 ml. of 0.5 per cent solution of 8-quinolinol in chloroform. The pH of the aqueous solutions was varied. The extraction time was also varied. The absorbances of the equilibrated chloroform layers were measured against the absorbance of an unextracted 0.5 per cent solution of 8-quinolinol in chloroform on a Cary Model 12 recording spectrophotometer.

The pH range for the most complete extraction of aluminum was 4.8 to 5.1. An extraction time of 5 to 6 minutes was required for the most complete extraction of aluminum. The absorbance maximum of the spectrum of tris(8-quinolinolo)aluminum(III), was found to occur at a wave length of 385 millimicrons. This is in agreement with the findings of Margerum, Sprain and Banks (21).

Calibration curves

A calibration curve was obtained for tris(8-quinolinolo)aluminum(III) by preparing a series of solutions containing 30 ml. of 2.0 molar 3-sulfopropionate and varying known amounts of aluminum from 10 to 120 micrograms. The pH of each solution was adjusted to 5.0 and each was extracted for 6 minutes with 20 ml. of a 0.5 per cent solution of 8-quinolinol in chloroform. The absorbances of the equilibrated chloroform phases were measured against the absorbance of an extracted 0.5 per cent solution of 8-quinolinol in chloroform with a Cary Model 12 recording spectrophotometer at a wave length of 385

millimicrons. The plot of absorbance of the chloroform phase against micrograms of aluminum per 20 ml. of chloroform-8-quinolinol solution, conformed to Beer's law over the concentration range of 10 to 120 micrograms of aluminum per 20 ml. of chloroform-8-quinolinol solution.

Margerum, Sprain and Banks (21) found that trace amounts of iron which are always present in thorium samples and in reagents can be masked by complexing the iron(II) with 1,10-phenanthroline.

Calibration curves for tris(8-quinolinolo)aluminum(III) were obtained by preparing a series of solutions containing 0.2 gram of thorium, 20 ml. of 1,10-phenanthroline solution, 1 ml. of hydroxylammonium chloride solution, 14 ml. of 0.056 molar Enta solution, 25 ml. of 2.0 molar 3-sulfopropionate solution and varying known amounts of aluminum from 10 to 120 micrograms. One solution was prepared which contained no aluminum. This was used as a blank. The pH of each solution was adjusted to 5.0 and each was extracted for 6 minutes with 20 ml. of a 0.5 per cent solution of 8-quinolinol in chloroform. The absorbances of the equilibrated chloroform phases were measured against the absorbance of the chloroform layer that was equilibrated with the blank solution. Both a Cary Model 12 recording spectrophotometer and Beckman Model DU quartz spectrophotometer were used to measure the absorbances at a wave length of 385 millimicrons. These data are shown in Table 3.

Table 3

Absorbance of tris(8-quinolinolo)aluminum(III) as a function of micrograms of aluminum per 20 ml. of chloroform-8-quinolinol solution

Micrograms of Al	Absorbance
10	0.136, 0.141, 0.128
20	0.254, 0.243, 0.246
40	0.499, 0.495, 0.490
80	0.978, 0.979, 0.995
120	1.440, 1.445, 1.445

The plots of absorbance of the chloroform phase against micrograms of aluminum per 20 ml. of chloroform-8-quinolinol solution, conformed to Beer's law over the concentration of 10 to 120 micrograms of aluminum per 20 ml. of chloroform-8-quinolinol solution.

It was found that points fell off the calibration curves when aluminum was extracted from solutions in which 3-sulfopropionate was added prior to the addition of Enta. This further indicated that the order of addition of the masking agents to thorium is critical.

When the disodium salt of N,N,N',N'-tetrakis-(carboxymethyl)-1,2-cyclohexanediamine was substituted for Enta as a masking agent for thorium, it was found that highly dispersed emulsions were always formed upon the extraction of the aqueous solutions with chloroform-8-quinolinol solutions.

Recommended procedure

Add 14 ml. of a 0.056 molar solution of Enta to an unknown solution containing exactly 0.2 gram of thorium. Add 1 ml. of a 10 per cent solution of hydroxylammonium chloride, 20 ml. of a 0.1 per cent solution of 1,10-phenanthroline and 25 ml. of a 2.0 molar solution of 3-sulfopropionate. Dilute to exactly 80 ml. and adjust the pH to 5.0. Allow 15 to 20 minutes for complete formation of the tris(1,10-phenanthroline)iron(II) ion. Prepare a blank solution which contains all reagents in the same concentration and at the same pH. Transfer each solution to a 250-ml. separatory funnel and add exactly 20 ml. of a 0.5 per cent solution of 8-quinolinol in chloroform. Shake once, release the pressure, and then shake for 6 minutes. Allow the phases to separate for 2 minutes. Draw off the chloroform layer into a 25-ml., glass-stoppered Erlenmeyer flask containing about 1 gram of anhydrous sodium sulfate. Shake well and allow the solution to stand for about 10 minutes to insure dryness of the chloroform before measuring the absorbance on a spectrophotometer at 385 millimicrons.

A calibration curve is obtained by preparing a series of solutions containing exactly 0.2 gram of thorium and varying known amounts of aluminum from 10 to 120 micrograms. These solutions are treated as were the solutions above. The quantity of aluminum in the unknown solution is obtained from the calibration curve.

"Unknown" solutions were made up by adding various quantities of aluminum to solutions containing 0.2 gram of thorium. These solutions were treated as given in the recommended procedure. The results obtained on these samples are shown in Table 4.

From 10 to 120 micrograms of aluminum can be determined within ± 1 microgram. From 100 to 1200 parts per million of aluminum can therefore be determined in 0.2 gram of thorium. Larger samples of thorium cannot be analyzed for aluminum by this method.

Table 4

Results of analyses of "unknown" aluminum samples

Sample	Al present, micrograms	Al found, micrograms	Error, micrograms
1	63	62.5	-0.5
2	16	15	-1
3	33	34	+1
4	107	108	+1
5	66	67	+1
6	38	36	-2
7	86	87.5	+1.5

Interferences

To solutions containing 0.2 gram of thorium and 40 micrograms of aluminum, 100 micrograms of various metal cations were added. The solutions were treated as was outlined in the recommended procedure. The results are shown in Table 5.

Many common cations seriously interfered with the aluminum determination. As stated earlier, trace quantities of iron are masked by 1,10-phenanthroline and do not interfere. It was found that nickel and zirconium did not interfere significantly. Margerum, Sprain and Banks (21) stated that interferences caused by copper, cobalt and zinc, were eliminated by washing the chloroform-8-quinolinol extract with an alkaline cyanide solution.

An alkaline cyanide solution was made up by dissolving 40 grams of ammonium nitrate, 20 grams of potassium cyanide and 10 ml. of concentrated ammonium hydroxide in enough distilled water to make 1 liter. It was found, however, that interferences by copper, cobalt and zinc were not eliminated by washing the chloroform-8-quinolinol extracts with the alkaline cyanide solution.

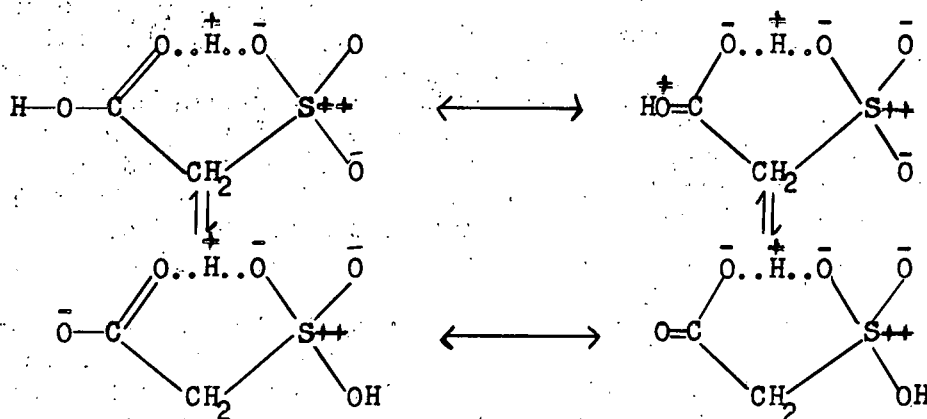
Table 5

Effect of various cations on the determination of aluminum

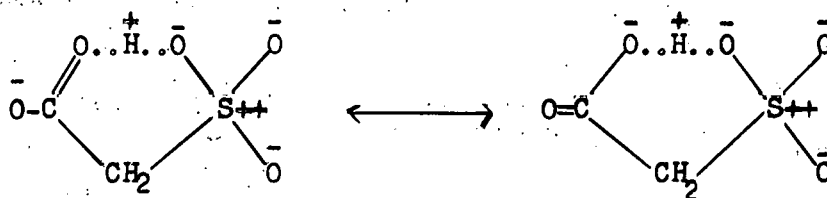
Cation	Al present, micrograms	Al found, micrograms	Error, micrograms
Fe(III)	40	41	1
Ti(IV)	40	46.5	6.5
Bi(III)	40	44	4
Mn(II)	40	46	6
Cr(III)	40	47	7
V(IV)	40	58	18
Ga(III)	40	62	22
Zr(IV)	40	40	0
In(III)	40	44	4
Ni(II)	40	42	2
Zn(II)	40	48.5	8.5
Co(II)	40	66	26
Cu(II)	40	73	33

The Values of K_{a2} for Sulfoacetic Acid and 3-Sulfopropionic Acid

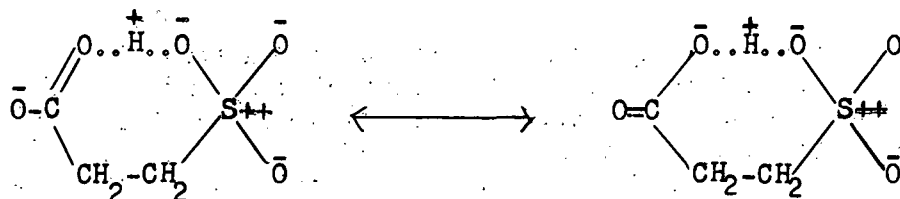
It was stated earlier that the ratios of the calculated to the experimental values of K_{a2} for sulfoacetic acid and 3-sulfopropionic acid were 885/1 and 25/1, respectively. Branch and Calvin (8, p.230) discussed the discrepancy between the calculated and experimental values of K_{a2} for sulfoacetic acid. They based their discussion upon experimental values of 5.8×10^{-3} and 8.9×10^{-5} for the K_{a1}' and K_{a2}' of sulfoacetic acid. These values of K_{a}' were probably obtained from Backer (2) but the value for K_{a1}' was apparently transcribed incorrectly since it was actually reported as 0.58. The value of 5.8×10^{-3} could hardly be the correct value since Smith (34) found that the sulfonic acid hydrogen in sulfoacetic acid is more highly dissociated in glacial acetic acid than is the first acid hydrogen of sulfuric acid. Furthermore, potentiometric titrations which were reported in this paper, revealed that the first hydrogen of sulfoacetic acid is completely titrated at a pH of 2 to 2.6. Branch and Calvin (8, p. 230) suggested the tautomeric equilibria shown below to explain the abnormally low value of 5.8×10^{-3} for K_{a1}' and the discrepancy between the calculated and experimental values of K_{a2} .



Since the reported value of 0.58 for K_{a1}' of sulfoacetic acid does not seem to be abnormally low, the structures below are probably the correct ones.



A similar chelation is postulated for 3-sulfopropionic acid.



Infrared spectra revealed the presence of intramolecular hydrogen bonds in sulfoacetate and 3-sulfopropionate. The difference in hydrogen bond strengths can lead one to predict readily that the discrepancy between the calculated and experimental values of K_{a2} will be greater for sulfoacetic acid than for 3-sulfopropionic acid.

The presence of intramolecular hydrogen bonding may not be the only factor contributing to the discrepancies. Branch and Calvin assumed that in the sulfonate group, the sulfur-oxygen bond was a single bond, that the sulfur atom had a formal positive charge of two, and that each oxygen atom had a formal negative charge of one. It has been stated (5, 19, 20, 24, 26, 27) that sulfur-oxygen bonds in compounds such as SO_2 , R_2SO_2 and SO_3 display much double bond character. The positive charge on sulfur in such compounds should lie between 0 and 1.0. Moffitt (24) calculated charges of 0.48 and 0.90 for the sulfur atoms in SO_2 and SO_3 , respectively. Pauling (26) calculated the same charges to be 0.46 and 0.71. The charge on sulfur in RSO_3 , using the Pauling treatment was calculated to be 0.71. As a generalization, the effective charge on sulfur in the sulfonate group probably lies between 0.5 and 1.0.

It is therefore proposed that the sulfonate group be treated as a resonating group. Branch and Calvin stated that a resonating group should be considered as one inductive unit and that one inductive constant should be applied to the entire group. If a charge of from 0.5 to 1.0 for sulfur is assumed, the inductive constant for the sulfonate group is between 7.3 and 11.2. On this basis, the calculated values of K_{a2} for sulfoacetic acid are between 1.10×10^{-3} and 5.75×10^{-3} and between 7.41×10^{-5} and 1.70×10^{-4} for 3-sulfopropionic acid. The ratios of the calculated to the observed values of K_{a2} are 12.8/1 to 67/1 for sulfoacetic acid and 2.5/1 to 5.7/1 for 3-sulfopropionic acid.

Limitations of Sulfoacetic Acid and 3-Sulfopropionic Acid as Masking Agents for Thorium

The only advantage that sulfoacetic acid or 3-sulfopropionic acid has over acetic acid as a masking agent for thorium is that neither of the former is extracted from an aqueous solution at pH 5.0 into chloroform-8-quinolinol solutions. Sulfoacetic acid and 3-sulfopropionic acid are stronger acids than acetic acid and both are less soluble in aqueous solution at pH 5 than is acetic acid. They are, therefore, less effective masking agents for thorium than is acetic acid.

When aqueous solutions containing sulfoacetate were extracted with chloroform-8-quinolinol solutions, highly dispersed emulsions were formed. It is postulated that the formation of strong intramolecular hydrogen bonds in sulfoacetate might contribute to the tendency of the compound to encourage the formation of emulsions. The hydrogen-bonded chelate might be less polar than the straight-chained acid. A less polar system will in general tend to encourage the formation of emulsions.

3-Sulfopropionate by itself could mask only small quantities of thorium. Because of the need for an analytical method in which 0.2 to 1.0 gram of thorium could be analyzed for aluminum, Enta was employed to aid 3-sulfopropionate in the masking of thorium. Even with the utilization of Enta, 0.2 gram of thorium was the largest sample that could be successfully masked. Larger samples of thorium would require the utilization of huge volumes of 3-sulfopropionate solution.

The recommended procedure can be used to determine 10 to 120 micrograms of aluminum in 0.2 gram of thorium to within 1 microgram. The procedure cannot be used to determine less than 100 parts per million of aluminum in 0.2 gram of thorium. The procedure must be carefully followed in order to obtain accurate results. Each solution in a given series of solutions must contain the same quantity of thorium. This is true because a slight quantity of thorium is extracted from the blank solution and this quantity will vary with slight differences in the quantity of thorium present. The reagents must be carefully added and the order of addition of reagents must be strictly adhered to. The pH of solutions to be extracted should be kept between 4.8 and 5.1.

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