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I. DETERMINATION OF MERCAPTANS
II. ION EXCHANGE SEPARATIONS USING SULFOSALICYLIC ACID

by

Thomas Adolph Palmer

A Dissertation Submitted to the
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PART I. DETERMINATION OF MERCAPTANS

INTRODUCTION

Numerous methods have been proposed for the determination of mercaptans. Two of the difficulties of these procedures are the lack of versatility and specificity.

The purpose of this investigation was to develop a rapid, accurate method for the determination of mercaptans.

The mercaptan-containing sample is titrated in neutral aqueous or acetone medium with mercury(II) perchlorate.

$$Hg^{++} + 2\ RSH \longrightarrow (RS)_2\ Hg + 2H^{+}$$

The end point is detected with a visual indicator or potentiometrically. Smaller amounts of mercaptans in hydrocarbon solution are titrated photometrically.

SURVEY OF THE LITERATURE

Mercaptans are chiefly characterized by their ease of salt formation (mercaptides) and by their ready oxidation to the corresponding disulfides. Dal Nogare (1) has reviewed the methods of mercaptan analysis.

Iodine is commonly used as an oxidant in the determination of mercaptans.

$$I_2 + 2RSH \longrightarrow RSSR + 2HI$$

However, this general method is restricted in its applications. Secondary mercaptans are more slowly oxidized than primary mercaptans (2). The oxidation products of secondary mercaptans are dependent upon the mercaptan concentration (3). In some cases, tertiary mercaptans are not quantitatively oxidized to sulfenyl iodide (4).

Organic copper salts have been used for the determination of mercaptans (5, 6).

$$2Cu^{++} + 4RSH \longrightarrow 2CuSR + RSSR + 4H^{+}$$

The end point is detected by the excess of copper(II) titrant. In the case of copper(I) mercaptide precipitation, an appreciable blank determination must be run. Some mercaptans cannot be determined because complex species formation prevents control of the reaction products.

Silver nitrate is commonly employed as a reagent in the analysis of mercaptans. Borgstrom and Reid (7) proposed the precipitation of silver mercaptide as an analytical method. The measured excess silver(I) is titrated by the Volhard method. Several shortcomings of this procedure are known. The silver mercaptide precipitate tends to occlude a considerable amount of silver ion, leading to high results. Also the formation of stable emulsions in the course of analysis is common. Malisoff and Anding (8) improved the silver nitrate procedure by the addition of methanol which solubilizes the silver nitrate in the hydrocarbon sample solvent and reduces the tendency to form emulsions and mercaptide agglomerates.

Tamele and Ryland (9) described the potentiometric determination of mercaptans with silver ion. The titration is followed using a silver wire indicating electrode and an electrolytic bridge to a mercury reference electrode. The use of alcoholic solutions eliminates the problem of silver ion adsorption. Bromide and iodide interfere, but chloride does not and can be determined by continuing the titration to a second potentiometric end point.

Kolthoff and Harris (10) reported the amperometric titration of mercaptans with silver nitrate, using the rotating platinum electrode. The addition of ammonium hydroxide greatly reduces the interference from chloride. Small amounts of bromide can be tolerated. This method tends to yield results which are slightly low, presumably because of air oxidation of the mercaptan to the disulfide. Strafford _et_ _al_. (11) showed that the use of a nitrogen blanket and oxygen-free reagents in the procedure resulted in nearly theoretical recovery of known amounts of mercaptans.

Kunkel _et_ _al_. (12) titrated aliphatic mercaptans with silver ion in an ammoniacal alcoholic medium, using ammonium dithizonate as indicator. Milligram amounts of chloride ion do not interfere. Higher amounts of chloride were not tested.

Sampey and Reid (2) determined mercaptans utilizing their reaction with mercury(II) chloride. The liberated hydrochloric acid is titrated to a methyl red end point. This method has the disadvantage that the acidic solution at the end point leads to slightly low results. Titration to a higher pH is impossible, since mercury(II) oxide will precipitate, thereby invalidating the titration.

Kolthoff _et_ _al_. (13) titrated the sulfhydryl group in biological substances with mercury(II) amperometrically. In some cases, the titration with mercury is more accurate and less sensitive to pH than the amperometric silver method.

Przbylowicz and Rogers (14) titrated mercaptans coulometrically using electrolytically generated mercury(II) titrant.

Granatelli (15) used a mercury(II) acetate titrant and dithizone indicator in the determination of microgram quantities of sulfur. Small amounts of olefins introduce appreciable error.

Kundu and Das (16) estimated the purity of mercaptans by the addition of a known amount of mercury(II) acetate to the sample. The excess acetate is titrated with hydrochloric acid. Thiophene, unsaturated compounds, and phenols interfere. Unsaturated compounds and phenols are tolerable if phenylmercury(II) acetate is used in place of mercury(II) acetate.

Gregg _et al_. (17) determined mercaptans by titration with mercury(II) nitrate using s-diphenylcarbazone as the indicator. The optimum pH range for successful titrations is 3.0 to 3.3. Halide ions must be absent.

Obtemperanskaya _et al_. (18) analyzed mercaptans by reacting them with excess acrylonitrile. Sodium sulfite is added and the alkali formed is titrated with hydrochloric acid. Some mercaptans have to react one hour before the actual determination.

Saville (19) utilized the reaction of silver nitrate with mercaptans in aqueous pyridine solution to determine the sulfhydryl group. The pyridinium nitrate formed is titrated with standard alkali. No potential interferences were studied.

EXPERIMENTAL

Development of the Method

Choice of titration solvent

The basis for the selection of the proper solvent was the solubility of the mercaptans and resulting mercury(II) mercaptides. Precipitation during titrations can lead to false end points which gives inaccurate results.

For water-insoluble mercaptans ethyl alcohol was considered as the titration solvent because of the chemical similarity of alcohols and mercaptans. However, in some determinations precipitation of mercury mercaptide occurred in the course of the titration. Dimethylformamide as a solvent reduced the end point sharpness and yielded low mercaptan results.

Acetone was adopted as the titration solvent. It possesses excellent solvating power for mercaptans and for the corresponding mercury salts. Of those mercaptans titrated, only the mercury salts of long-chained alkyl mercaptans precipitated.

Since the determination of mercaptans in gasoline is an important one, their titration in mixed hydrocarbon-acetone solvent was tested. Using either benzene or petroleum ether

(65-110°C), it was found that a higher ratio than 40 volume per cent hydrocarbon led to annoying emulsions which obscured the end point.

Water-soluble mercaptans are preferably titrated in aqueous solution. There were some cases of mercury mercaptide precipitation in acetone.

The sharpness of the end point using the visual indicator method compared favorably in acetone, water, and hydrocarbon-acetone solvents.

Pyridine acts as a buffer in the pH range of 5 to 6. In acidic solution, thio-Michler's ketone indicator is easily oxidized and in basic solution mercury(II) oxide precipitates. The formation of a weak mercury(II)-pyridine complex tends to improve the solubility of the mercaptide salts.

Choice of titrant solvent

The determination of mercaptans in acetone or water is satisfactory using an aqueous mercury(II) perchlorate titrant. Attempts to prepare a non-aqueous titrant for the analysis of mercaptans in hydrocarbon solvents were made.

Acidified mercury(II) perchlorate was not soluble in methyl iso-butyl ketone, methyl ethyl ketone, acetic acid, or tert-butyl alcohol.

Solutions of mercury(II) in iso-propyl alcohol and in ethyl alcohol developed grey-black residues upon standing. Mercury(II) oxidizes the alcohols to the corresponding carbonyl compounds.

Dimethoxyethane was rejected because the peroxides in this solvent will easily oxidize the mercaptans analyzed.

A solution of mercury(II) perchlorate in acetonitrile was clear and colorless. However, the molarity of the solution decreased about 0.4 per cent per day. Qualitatively mercury(I) was found in this titrant.

The aqueous titrant was subsequently used for all analyses.

Detection of the end point

Gehauf and Goldenson (20) found that thio-Michler's ketone, 4,4'-bis(dimethylamino)thiobenzophenone forms highly colored compounds with trace amounts of copper(I), mercury(II), gold, silver, platinum, and palladium in acetate medium. They reported the colorimetric determination of mercury. The volumetric analysis of cyanide by titration with mercury(II) is successful using thio-Michler's ketone as an internal indicator. The presence of chlorides do not interfere.

Fritz and Sutton (21) titrated mercury with bis(2-hydroxyethyl)dithiocarbamate. Thio-Michler's ketone indicator gives a very sharp end point. However, the sharpness is decreased in the presence of chloride ion.

Macro-amounts of mercaptans are analyzed with mercury(II), using either thio-Michler's ketone as a visual indicator or potentiometrically with the mercury indicator electrode.

Reilley and Schmid (22) have described the theoretical principles concerning the use of mercury as a pM indicator electrode in chelometric titrations.

Miller and Hume (23) used the mercury electrode in the determination of mercury(II), copper(II), and gold(III). These cations are titrated coulometrically using electrolytically generated mercaptoacetic acid.

Milligram quantities of mercaptans in hydrocarbon solvents were titrated photometrically. The principles of the photometric titration method have been reviewed (24).

The titration of mercaptans was followed at a wave length of 580 mμ, which is the wave length of maximum absorbance for the thio-Michler's ketone-mercury(II) complex (20). The free indicator does not absorb at this wave length.

Apparatus

pH meter: All potentiometric titrations were performed on a Beckman Model G pH meter equipped with a J-type mercury electrode (25) and a Beckman 1170 calomel reference electrode.

Spectrophotometer: A Beckman Model B spectrophotometer as modified by Fritz and Pietrzyk (26) was used for the photometric titrations.

Glassware: Kimble "Kimax" burets were used for all titrations throughout this work. All volumetric glassware was Class A.

Reagents

Mercury(II) perchlorate, 0.05 M. Approximately 26 grams of mercuric perchlorate trihydrate (G. Frederick Smith Chemical Co.) was dissolved in one liter of 0.1 M perchloric acid. The resulting solution was filtered. The mercury(II) solution was standardized with 0.05 M EDTA [disodium dihydrogen(ethylenedinitrilo)tetraacetate] at pH 6 using either methylthymol blue (27) or thio-Michler's ketone indicator. Less concentrated solutions were prepared by dilution with 0.1 M perchloric acid.

4,4'-Bis(dimethylamino)thiobenzophenone (thio-Michler's ketone). An approximately 0.01% solution of the Eastman white label chemical was prepared in acetone immediately before use.

Mercaptan samples. Analyzed as received.

All other chemicals were reagent grade or equivalent.

Procedures

Visual indicator method

The sample containing 0.3 to 1.0 mmole of mercaptan was weighed into a 250-ml. Erlenmeyer flask containing 100 ml. of solvent. One ml. of pyridine and 10 drops of the indicator solution were added. The mercaptan was titrated with a 0.05 $\underline{M}$ mercury perchlorate delivered from a 10-ml. buret. The end point was the color change from yellow to blue.

Potentiometric method

The sample containing 0.3 to 1.0 mmole of mercaptan was weighed into a 250-ml. beaker containing 125 ml. of solvent. One ml. of pyridine was added. The titration with 0.05 $\underline{M}$ mercury(II) was followed potentiometrically using the mercury indicator electrode and the saturated calomel reference electrode. The equivalence point was determined by plotting potential against the volume of titrant.

Photometric method

A 25-ml. or smaller aliquot of hydrocarbon solvent containing 0.006 to 0.5 mmole of mercaptan was pipetted into a 180-ml. electrolytic beaker. One ml. of pyridine and one ml. of thio-Michler's ketone solution were added. The solution was diluted to 100 ml. with acetone. The beaker was placed in the spectrophotometer cell compartment. A 10-ml. buret containing 0.00005 M to 0.01 M mercury(II) perchlorate was inserted into the solution. The stirrer was turned on. The absorbance was set to zero and the wave length was set at 580 mμ. Titrant was added in 0.5 ml. increments; just after the equivalence point, titrant was added in three or four increments of 0.05-ml. The end point was determined graphically plotting absorbance against the volume of titrant. An indicator blank was determined on the more dilute mercaptan samples.

RESULTS AND DISCUSSION

Table 1 presents the results for the determination of various mercaptans, using the visual indicator method. The purity of many of the compounds was checked iodimetrically (28).

The titration is applicable to virtually all types of mercaptans: aliphatic including primary, secondary and tertiary, aromatic, dimercapto-compounds, and mercaptans containing other functional groups. Of the compounds analyzed, only the titration of 2-mercaptobenzothiazole failed.

Representative curves for the potentiometric titration of mercaptans are plotted in Figure 1. In these titrations the potentiometric and the visual indicator end points agree within 0.2%. An outstanding feature of the titration curves is the sharpness of the break at the end point.

The potentiometric titration of 80% mercaptoacetic acid and 2-mercaptoethanol gave one break equivalent to the total sulfhydryl content. A differentiating titration of 4-toluenethiol and 2-benzoxazolethiol was performed. However, the results were not quantitative.

The spectrophotometric titration of mercaptans was undertaken for two reasons. The indicator and the potentiometric methods failed to give accurate, precise analyses for samples

Table 1. Analysis of mercaptans

Mercaptan	Per cent purity ±average deviation	iodimetric
1-Octanethiol	96.0±0.2	96.0
t-Octyl mercaptan	93.1±0.2	fails
1-Decanethiol	97.1±0.1	97.2
1-Octadecanethiol	95.5±0.4	95.5
2-Mercaptoethanol	97.2±0.5	98.6
1-Mercaptopropane-2,3-diol	89.2±0.1	
Mercaptoacetic acid, 70%	68.3±0.1	69.0
Mercaptoacetic acid, 80%	78.6±0.0	
Isooctyl mercaptoacetate (mixed isomers)	97.3±0.1	97.5
3-Mercaptopropionic acid	98.6±0.2	
Mercaptosuccinic acid	90.5±0.6	
Glycol dimercaptoacetate	95.0±0.2	
2-Diethylaminoethanethiol hydrochloride	93.6±0.1	94.1
4-Chlorothiophenol	97.1±0.4	97.3
Pentachlorothiophenol	94.1±0.3	
4-t-Butylthiophenol	98.7±0.3	
Toluenethiol (mixed isomers)	93.1±0.0	
Xylenethiol (mixed isomers)	72.8±0.2	72.8
Benzyl mercaptan	98.8±0.5	
2-Benzoxazolethiol	98.8±0.0	
Thionalide	93.4±0.2	fails

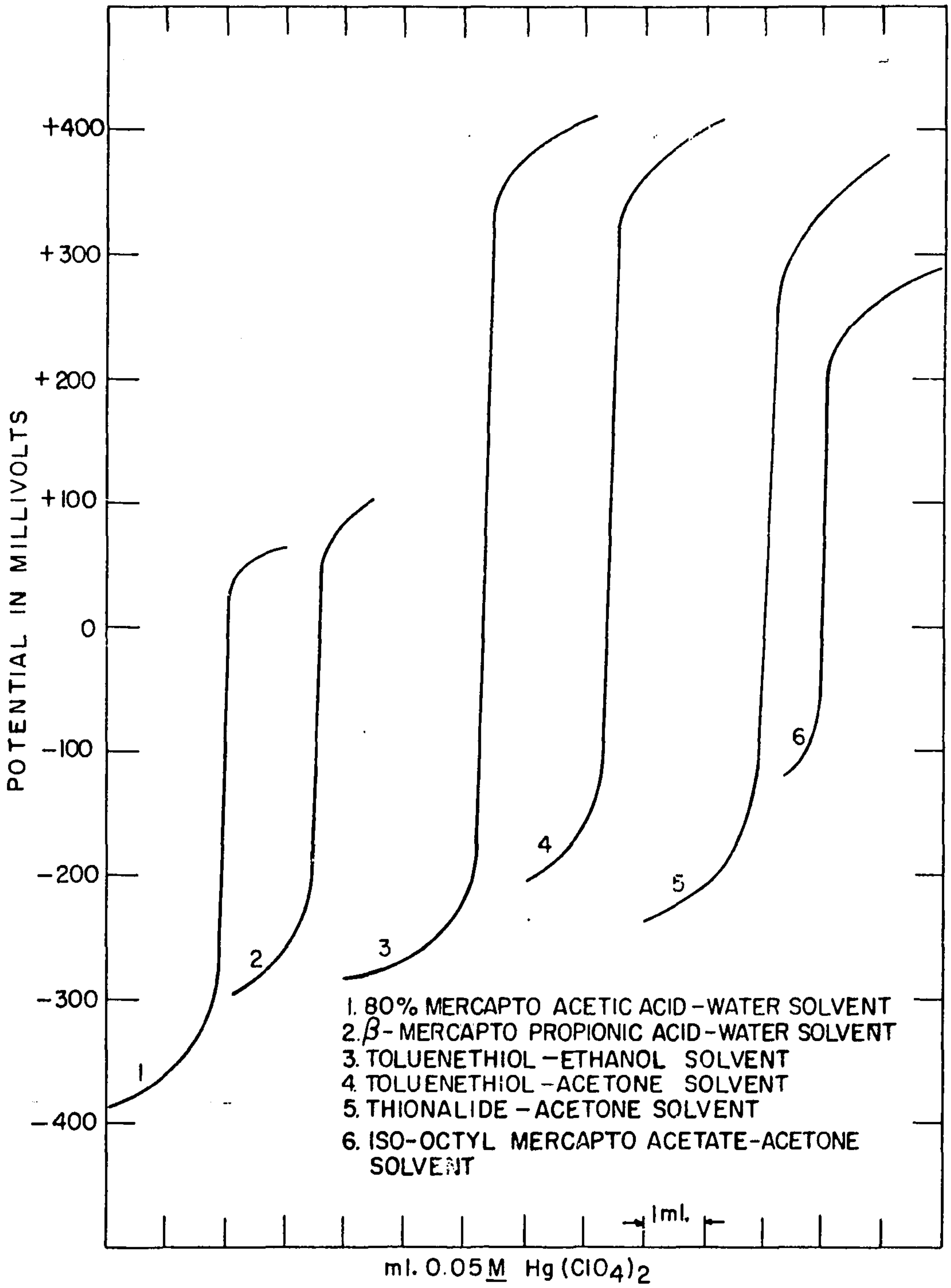


Figure 1. Potentiometric titration of mercaptans

containing less than 0.03 mmole of mercaptan. The determination of small amounts of mercaptans in petroleum is of considerable importance because of their deleterious properties.

Table 2 gives the results of the photometric titration of mercaptans. The theoretical titration values were obtained using the visual indicator method. The average error for all the titrations is 0.5%. The effect of titrant concentration upon the slope of the titration curve is shown in Figure 2.

Table 2. Photometric titration of mercaptans

Mercaptan	$Hg(ClO_4)_2$ M	Milligrams mercaptan Taken	Milligrams mercaptan Found	Difference
Isooctyl mercapto-acetate	0.00236	4.57	4.60	+0.03
	0.00471	9.80	9.87	+0.07
	0.00942	17.25	17.33	+0.08
1-Octanethiol	0.000538	0.879	0.876	-0.003
	0.00134	1.82	1.83	+0.01
	0.00269	3.78	3.79	+0.01
	0.00538	5.94	5.96	+0.02
	0.0108	14.06	14.04	-0.02
1-Decanethiol	0.00134	1.78	1.77	-0.01
	0.00269	4.31	4.30	-0.01

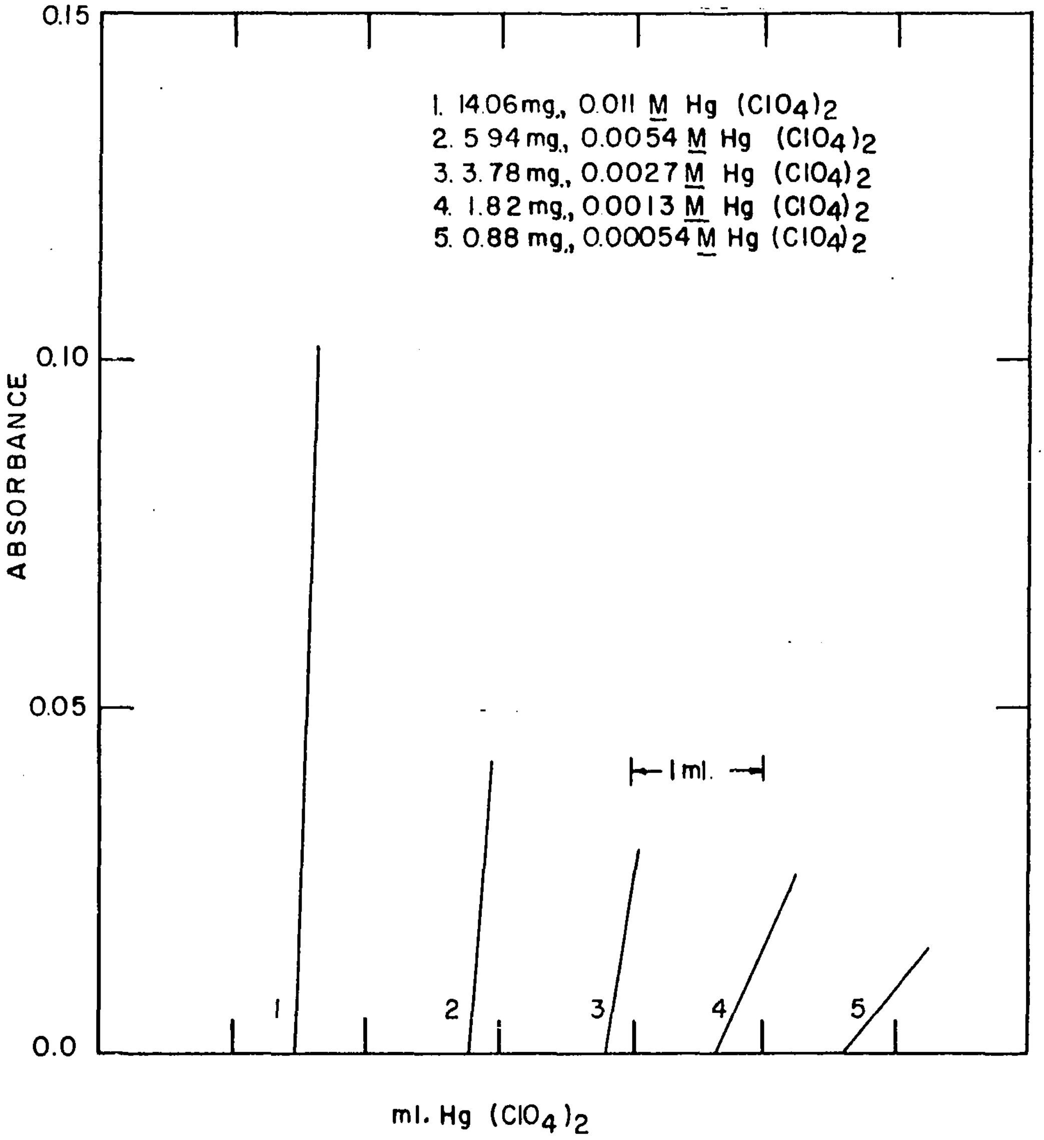


Figure 2. Photometric titration of 1-octanethiol

The photometric titrations were performed in mixed petroleum ether-acetone solvent. Presumably gasoline solutions of mercaptans can be titrated in the place of the petroleum ether solutions.

The equilibrium past the end point was rather slow. Stable absorbance readings were obtained within ten minutes after the addition of an increment of titrant. Only three or four absorbance readings were necessary to establish a workable titration curve.

An extensive interference study in the determination of mercaptans is presented. The compounds investigated included compounds that react with mercury(II) or with mercaptans, compounds which interfere in existing methods of mercaptan analysis, and compounds containing other sulfur functional groups. The visual indicator method was used in the determination of the mercaptans.

The effect of potential interferences upon the determination of 3-mercaptopropionic acid is summarized in Table 3. Fluoride in 100 to 1 molar ratio and chloride in 200 to 1 ratio do not interfere in the analysis of the mercaptan. Large amounts of bromide interfere seriously in existing methods using silver ion titrant. Amounts up to 12.5 millimoles of bromide do not interfere in the proposed method. Larger amounts reduce the sharpness of the end point.

Table 3. Analysis of 3-mercaptopropionic acid in the presence of potential interferences

Interference-mmoles		Millimole mercaptan		Per cent
		Taken	Found	recovery
Sodium fluoride	50	0.503	0.500	99.5
	50	0.525	0.524	99.9
Sodium chloride	100	0.558	0.559	100.2
	100	0.592	0.588	99.3
Sodium bromide	12.5	0.557	0.551	99.0
	12.5	0.502	0.511	101.7
	25	0.582	0.582	100.0
Dimethyl sulfoxide	26.4	0.515	0.509	98.8
	25.0	0.527	0.525	99.6
Benzenesulfonic acid	9.6	0.501	0.499	99.6
	13.8	0.513	0.512	99.8
Acetonitrile	113	0.514	0.517	100.6
	101	0.532	0.534	100.4
	262	0.477	0.488	102.3
	253	0.524	0.534	101.9
Potassium hydrogen acetylenedicarboxylate	5.0	0.519	0.516	99.4
	5.0	0.559	0.558	99.9
	12.5	interferes		
Thiodiglycolic acid	5.0	0.523	0.518	99.1
	5.0	0.533	0.534	100.1
	12.5	interferes		

Dimethyl sulfoxide in 50:1 molar ratio and benzenesulfonic acid in 25:1 ratio are tolerable in the determination of 3-mercaptopropionic acid. Thiodiglycolic acid, an alkyl sulfide, is tolerable in 5 millimole concentration. A 25 to 1 molar ratio of thiodiglycolic acid to mercaptan is not tolerable because a mercury(II) precipitate forms during the course of the titration.

Potassium cyanide interferes seriously in the analysis of mercaptans. Acetonitrile, however, is tolerable in 200 to 1 ratio with mercaptan. Higher amounts cause slightly high results in the mercaptan analysis.

Unsaturated compounds are not tolerable in the iodimetric method of mercaptan determination. Potassium hydrogen acetylenedicarboxylate in 10 to 1 molar ratio does not affect the results of 3-mercaptopropionic acid. In the titration of the mercaptan in the presence of 12 millimoles of unsaturated compound, a precipitate formed which invalidated the analysis.

The results of the analyses of 4-t-butylthiophenol in the presence of three sulfur-containing compounds are in Table 4. Large amounts of thiophene do not affect the mercaptan determination.

Diphenyl disulfide is tolerable in 3 millimole level in the analysis of mercaptans. Higher amounts react with the in-

Table 4. Analysis of 4-t-butylthiophenol in the presence of potential interferences

Interference-mmoles		Millimole mercaptan		Per cent recovery
		Taken	Found	
Thiophene	25.4	0.440	0.440	100.0
	25.0	0.421	0.422	100.2
Diphenyl disulfide	2.5	0.532	0.524	98.5
	2.5	0.441	0.440	99.8
	5.0	interferes		
Diphenyl sulfide	13.9	0.433	0.433	100.0
	14.0	0.420	0.422	100.3

dicator. Diphenyl sulfide in large amounts does not interfere. Mercury(II) salts have been used to characterize organic sulfides (29).

The effect of added compounds upon the analysis of isoocytl mercaptoacetate is presented in Table 5.

1,2-Dichlorobenzene and 1,2-dibromoethane are tolerable in 100 to 1 ratios. Carbon disulfide in 200 to 1 ratio with mercaptan does not interfere. Mercaptan samples containing more than four millimoles of sulfadiazine were not tested because of its relative insolubility in acetone.

Moderate amounts of styrene do not interfere in the determination of isooctyl mercaptoacetate. This is significant

Table 5. Analysis of isoocytl mercaptoacetate in the presence of potential interferences

Interference-mmoles		Millimole mercaptan taken	Millimole mercaptan found	Per cent recovery
1,2-Dichlorobenzene	51.9	0.424	0.424	100.0
	54.3	0.529	0.526	99.4
1,2-Dibromoethane	53.9	0.497	0.496	99.8
	51.8	0.511	0.511	100.0
Dibutyl sulfide	25.0	0.458	0.457	99.8
	24.7	0.483	0.480	99.4
Carbon disulfide	112	0.490	0.489	99.8
	91.1	0.533	0.531	99.6
Sulfadiazine	3.4	0.470	0.471	100.2
	3.5	0.474	0.475	100.2
Styrene	5.6	0.509	0.513	100.8
	5.0	0.490	0.492	100.4
	13.5	0.461	0.476	103.3
	12.9	0.524	0.537	102.5
1,2-Epoxyethylbenzene	58.2	0.445	0.444	99.8
	52.3	0.499	0.499	100.0
3-Methyl-1-pentyn-3-ol	4.8	0.505	0.510	101.0
	5.2	0.474	0.478	100.8
	13.4	0.510	0.521	102.2
	13.0	0.499	0.507	101.6

because mercury(II) acetate adds quantitatively to the double bond in styrene (30). 1,2-Epoxyethylbenzene in large amounts does not interfere. This compound has been determined using dodecanethiol (31).

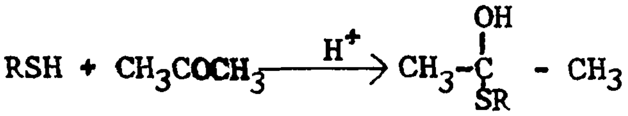
The following compounds interfere in the analysis of mercaptans due to their reaction with mercury(II): potassium cyanide, potassium iodide, sodium sulfide, thiourea, acetyl thiourea, potassium ethylxanthate, sodium diethyldithiocarbamate, thioacetamide, dithiodibenzoic acid, and bis(dimethylthiocarbamyl)disulfide.

Sulfur in the absence of added mercaptans does not react with mercury(II). Heavy precipitation occurs in a solution of sulfur and mercaptan upon the addition of mercury(II) solution. Sulfur reacts with the mercaptan to form polysulfide species which reacts with mercury to precipitate mercury(II) sulfide (32).

Halides interfere in the potentiometric determination of mercaptans. The formation of insoluble mercury(I) halides limits the potential of the mercury indicator electrode (22).

The influence of strongly acidic or basic solutions upon the determination of mercaptans was studied. For analysis in aqueous systems, solutions were neutralized to pH 5 to 7 and the visual indicator procedure was followed to give accurate results.

Low non-reproducible results were obtained in the titration of mercaptans in acetone solutions which are highly acidic. This was caused by the acid-catalyzed reaction of mercaptan with acetone to give the corresponding mercaptal.



$$RSH + CH_3COCH_3 \xrightarrow{H^+} CH_3-\overset{\displaystyle OH}{\underset{\displaystyle SR}{C}} - CH_3$$

Mercaptals are unreactive toward alkali and are not readily hydrolyzed by acids (33). To obtain accurate results, mercaptan solutions of high acid content were neutralized in a nonketone, e.g. ethyl alcohol, before the addition of acetone and the titration of the mercaptan.

SUMMARY

The determination of mercaptans by titration in acetone or aqueous solution with mercury(II) perchlorate has been proposed. The end point is detected visually using thio-Michler's ketone indicator. Alternately, the titration is followed potentiometrically with a mercury indicator electrode and a saturated calomel reference electrode.

Milligram amounts of mercaptans in hydrocarbon solvents are titrated photometrically.

Large amounts of chloride, bromide, and acetonitrile do not interfere in the analysis of mercaptans. Most sulfur-containing organic compounds are tolerable. Significant amounts of unsaturated compounds do not affect the results. The important interferences are elemental sulfur, sulfide, iodide, cyanide, and thiocarbonyl compounds.

Acidic solutions of mercaptans must be neutralized prior to the addition of acetone to prevent mercaptal formation which leads to low results.

PART II. ION EXCHANGE SEPARATIONS USING SULFOSALICYLIC ACID

INTRODUCTION

The use of ion exchange in chemical analysis has become extremely widespread in recent years. The applications of ion exchange may be classified as follows: concentration of dilute solutions, fractionating of ions having similar analytical properties, and removal of interfering ions. The chief advantage of an ion exchange technique is the simple and rapid achievement of a separation or concentration that would ordinarily be very difficult and time-consuming. Monographs (34, 35) and articles (36-39) have appeared which review the aspects of ion exchange of particular interest to the analytical chemist.

Ion exchange separation methods may be classified into two groups. The first of these is ion exchange chromatography. This technique involves the separation of ions from each other owing to differences in their resin affinities. The best illustration of this method is the classic work of Spedding and associates (40). Spedding separated the individual rare earths on cation exchange resin by selective elution using a dilute solution of citric acid.

Of greater importance to analytical chemists is the work of Kraus and coworkers, (41). They investigated all cations for their ability to form anion complexes in hydrochloric acid solution. They found that by adjusting the hydrochloric acid concentration, many ions normally difficult to separate are readily separated on anion exchange resin.

The second method of ion exchange separations is called the single-pass method. In this technique the separation is effected by simply passing the appropriately prepared sample through the ion exchange resin. One or more components are retained by the resin phase, and the others pass through the column. The single-pass method is accomplished by the use of complexing agents. The requirements for a separation of a binary mixture on cation exchange resin are that one component forms an uncharged or negatively charged complex and that the other exists as a cation.

Ustrenko and Datsenko (42) separated calcium and magnesium from aluminum and iron on cation exchange resin using tartaric acid to form anion complexes with aluminum and iron. EDTA has been frequently employed as a complexing agent in single-pass separations. Fritz and Umbreit (43) resolved mixtures of lanthanum-thorium, samarium-iron, and ytterium-scandium, using EDTA at a strictly controlled pH to elute thorium, iron, and scandium, respectively. Taketatsu (44) separated bismuth from cadmium, zinc, and lead on cation exchange resin with EDTA. Citrate-form anion exchange resin separates calcium from aluminum and iron (45). Iron and aluminum are eluted with varying concentration of hydrochloric acid.

The technique described in this investigation is the extension of the single-pass ion exchange using sulfosalicylic acid as a selective agent. To accomplish a separation, an excess of sulfosalicylic acid is added to the metal ion solution. The solution is buffered at a pH where the sulfosalicylate complex of one metal is formed, while the complex of the other metal is largely dissociated. The solution is passed through a previously buffered column of cation exchange resin. The uncomplexed metal is retained by the resin and the complexed metal passes quantitatively through the column.

Tompkins and Mayer (46) studied several complexing agents in their determination of the optimum conditions for the separation of europium and promethium on cation exchange resin. Sulfosalicylic acid compares favorably with citric acid as an eluting agent in this separation.

Schubert *et al*. (47) separated beryllium from copper and from uranium using cation exchange chromatography. pH 3.5 sulfosalicylate elutes beryllium and 3 *M* sulfuric acid removes the copper. In the beryllium-uranium separation sulfosalicylate at pH 3.5 to 3.8 elutes the beryllium and the uranium is stripped with sulfosalicylate adjusted to pH 4.6-4.7.

Alimarin and Tsintsevich (48) separated gallium from zinc on cation exchange resin. Gallium is eluted with pH 10 sulfosalicylate while zinc is stripped from the resin with hydrochloric acid. Oliver and Fritz (49) separated several binary mixtures on both cation and anion exchange resins. Uranium, iron, thorium, aluminum, ytterium, zirconium, and bismuth form anionic complexes with pH 8-10 sulfosalicylate. Copper, zinc, nickel, and cadmium form cationic complexes with ethylenediamine at pH 8-10. Using pH 9.5 sulfosalicylate as an eluting agent, Szidon (50) separated iron and aluminum from copper, nickel, and zinc on chelating resin.

Ion exchange separations using the single-pass method have the advantages of simplicity and speed in comparison to the chromatographic technique. However, it is limited in that only two fractions are obtained: one which passes through the resin and the other which is retained by the resin phase. This ion exchange method is, nevertheless, a valuable tool in the separation of trace quantities of impurities from the major component of a sample.

EXPERIMENTAL

Apparatus

Glassware: Kimble "Kimax" burets were used for all titrations throughout this work. All volumetric glassware was Class A. Columns used in the ion exchange separations consisted of tubing 2.2 cm. inside diameter and 8 cm. in length, equipped with a coarse glass frit and a two-way stopcock. The columns were fitted with a rubber stopper holding a short stem filtering funnel which served as a reservoir. Similar columns of 12 cm. length were used in the case of the investigation of the effect of column length.

pH meter: All pH measurements were made on a Beckman Model G pH meter equipped with a Beckman 1190-80 glass electrode and a Beckman 1170 calomel electrode.

Spectrophotometer: The photometric titrations were performed on the modified Beckman Model B spectrophotometer (26).

Chromatography cabinet: A Chromatocab Model A 125 cabinet was used in the ion exchange paper chromatography studies.

Reagents

Ion exchange resin: J. T. Baker Chemical Company "Analyzed Reagent" Dowex 50W-X8, 100-200 mesh, sodium form, was used throughout the work. Regeneration was accomplished by the following procedure. Approximately 400 ml. of wet resin was placed in a large column and was backwashed with water to remove the fines. Two liters of 3 M hydrochloric acid was passed through the column. Two liters of water followed. 2000 grams of a ten per cent diammonium hydrogen citrate solution, adjusted to pH 3.0 to 3.5 with hydrochloric acid, was percolated through the resin. After a two-liter water rinse, the resin was converted to the sodium form with 2000 grams of a ten per cent sodium chloride solution. The resin was then washed with water until a test for chloride in the effluent was negative. The resin was filtered with suction and the excess water was removed by washing with ethyl alcohol and then with acetone.

Ion exchange papers: Reeve Angel Grade SA-2 ion exchange resin loaded paper was used. It is a strong acid cation exchanger containing about 55 per cent Amberlite IR-120 resin in the sodium form.

EDTA [disodium dihydrogen(ethylenedinitrilo)tetraacetate dihydrate]: Eastman white label grade.

Zinc metal: Primary standard zinc of 99.99 per cent purity from the Platt Brothers and Company, Waterbury, Connecticut.

All other chemicals were reagent grade.

Metal ion solutions, 0.05 *M*: Lanthanum(III), yttrium(III), and ytterbium(III) solutions were prepared by dissolving the respective oxides in perchloric acid. Titanium(IV) solution was prepared by dissolving titanium(IV) chloride in 0.5 *M* hydrochloric acid. Vanadium(IV) solution was prepared from vanadyl sulfate and zirconium(IV) was prepared from zirconyl chloride. All other metal ion solutions were prepared from the reagent grade nitrate or perchlorate salts.

Sulfosalicylic acid, 0.15 *M*: 1.52 grams of sulfosalicylic acid dihydrate was dissolved in 40 ml. of water.

Acetate buffer, 0.05 *M*: 5.10 grams of sodium acetate trihydrate was dissolved in 750 ml. of water. Approximately 13.5 ml. of 0.15 *M* sulfosalicylic acid was added and the pH was adjusted to the appropriate pH with dilute sodium hydroxide or perchloric acid. The resulting solution was 0.0026 *M* in sulfosalicylate.

Acetate buffer, 0.10 *M*: This solution was prepared similarly to that of 0.05 *M* acetate, except 10.2 grams of sodium acetate trihydrate was used.

Analytical Procedures

EDTA: EDTA solutions were standardized by titrating standard zinc(II) solution, using naphthyl azoxine (15) and

Briochrome Black T (27) as indicators.

Lanthanum(III), yttrium(III), and ytterbium(III): These metals were analyzed by an EDTA titration using arsenazo indicator (52).

Copper(II), cadmium(II), zinc(II), cobalt(II), lead(II), and nickel(II): These metal ions were determined by titration with EDTA using naphthyl azoxine indicator (51).

Aluminum(III): This metal was determined by backtitration of excess EDTA with zinc(II) perchlorate in 50 per cent ethyl alcohol using dithizone indicator (53).

Thorium(IV): Analysis of thorium was by EDTA titration using xylenol orange indicator (27).

Titanium(IV): This cation was analyzed by a backtitration of excess EDTA with copper(II) in the presence of hydrogen peroxide, using naphthyl azoxine S indicator (54).

Mercury(II): Analysis of mercury was performed by titration at pH 6 with thioglycerol (1-mercaptopropane-2,3-diol) solution, using thio-Michler's ketone indicator.

Manganese(II): This ion was determined by EDTA titration with Briochrome Black T indicator in the presence of ascorbic acid and potassium cyanide (55).

Magnesium(II): Titration of magnesium with EDTA was performed in the presence of ascorbic acid, triethanolamine, and potassium cyanide, using Eriochrome Black T indicator (55).

Uranium(VI): Analysis was by the oxidation-reducation method of Sill and Peterson (56).

Iron(III): Samples of iron were titrated photometrically at a wave length of 500 mμ with EDTA, using sulfosalicylic acid as indicator. The procedure is similar to that of Sweetser and Bricker (57).

Zirconium(IV): Gravimetric analysis of zirconium was performed using mandelic acid as the precipitant (58).

Vanadium(IV): Samples containing vanadium were analyzed by the method of Fritz et al. (54).

Ion Exchange Paper Chromatography of Metal Sulfosalicylates

In order to obtain the optimum pH conditions for ion exchange separations, the behavior of metal ions was investigated on ion exchange paper using sulfosalicylate as an eluant.

The procedure for the paper chromatography study of metal ions follows. Strips of ion exchange paper, 3.5 cm. x 30.5 cm., were placed in the troughs of the chromatography cabinet. A buffer solution, 0.2 M in ammonium acetate and 0.008 M in sulfosalicylate, of appropriate pH was placed in the troughs and allowed to percolate down the ion exchange paper overnight. The papers were then rinsed with water. Metal sulfosalicylate solutions were prepared by mixing 2 ml. of 0.05 M metal ion, 6 ml. of 0.2 M buffer, and 3 ml. of 0.17 M sulfosalicylic acid. The pH was adjusted with dilute ammonia or perchloric acid. Using a 200γ pipet, the samples were applied to the ion exchange papers 23 cm. from the bottom of the paper. The papers were loaded in the troughs and 0.2 M buffer was allowed to pass down the papers. A dry ion exchange paper was also placed in the trough to ascertain the distance moved by the eluant. After the eluant had reached the bottom of the paper (70 to 90 minutes), the papers were removed from the chromatograph cabinet and air-dried. Table 6 gives the qualitative tests used in determining the distance moved by the metal ions.

Separation of Metal Ion Mixtures

A slurry of Dowex 50W-X8, 100-200 mesh, sodium form resin, was poured into a column which contained approximately 5 ml. of water until the resin column was 4 cm. high. The water was allowed to drain until the water level above the resin was about 1.5 cm. The rubber-stoppered funnel was fitted into the column. 75 ml. of 0.05 M acetate buffer passed through the column at the rate of 8 to 13 ml./min. The pH of the effluent was measured. If it was within 0.05 pH unit of the desired value, the column was ready for use. In most cases the pH of the ef-

Table 6. Qualitative tests used in the paper chromatography study

Metal ion	Reagent	Conditions	Positive test
Iron(III)	sulfosalicylate	hydrochloric acid solution	red coloration
Uranium(VI)	arsenazo		purple coloration
Titanium(IV)	hydrogen peroxide	hydrochloric acid solution	yellow coloration
Zirconium(IV)	methylthymol blue	0.5 M HCl	yellow coloration
Cobalt(II)	2-nitroso-1-naphthol		brown stain
Lanthanum(III)	arsenazo		blue coloration
Thorium(IV)	arsenazo		blue coloration
Yttrium(III)	arsenazo		blue coloration
Copper(II)	sodium diethyldithiocarbamate		yellow coloration
Mercury(II)	thio-Michler's ketone		blue coloration
Zinc(II)	naphthyl azoxine		yellow coloration
Nickel(II)	dimethylglyoxime		red stain

fluent was not within this limit, so another 75 ml. of acetate buffer was passed through the column and the pH was again measured. The proper pH was always obtained after the second rinse of buffer had passed through the resin.

The binary mixture to be separated was prepared by placing 0.05 to 0.5 millimole of each metal ion in a beaker. To this was added an amount of 0.15 M sulfosalicylic acid equivalent to three times the molar concentration of total metal ion. 30 ml. of acetate buffer was then added and the pH was adjusted within 0.05 pH unit of the proper value with dilute sodium hydroxide or perchloric acid. The pH of titanium(IV) solutions was adjusted with dilute ammonia in order to prevent the hydrolysis of Ti(IV).

The sample was placed in the funnel above the column and was allowed to pass through the resin bed at the maximum rate of flow, which was 8 to 13 ml./min. When the liquid level dropped to the top of the neck of the funnel, a 30-ml. rinse of acetate buffer solution, which had been used to rinse out the sample beaker, was poured into the funnel. Three additional buffer rinses were similarly applied. The pH of the effluent solution was measured.

The metal which remained on the column was eluted with acid at a rate of 4 to 6 ml./min. 0.25 millimole or less of zinc(II), cobalt(II), nickel(II), manganese(II), and magnesium(II) was eluted with 150 ml. of 3 M hydrochloric acid. Larger amounts of these metal ions were eluted with 200 to 225 ml. of 3 M hydrochloric acid. Similar amounts of copper(II) and cadmium(II) were eluted with 1 M hydrochloric acid. Less than 0.25 millimole of lanthanum(III), yttrium(III), and ytterbium(III) was eluted with 350 ml. of 4 M hydrochloric acid. 475 ml. of 4 M hydrochloric acid was used to elute larger amounts of yttrium. Lead(II) was stripped from the resin with 150 ml. of 4 M nitric acid.

The effluents containing aluminum(III), titanium(IV), uranium(VI), vanadium(IV), zirconium(IV), and thorium(IV) were treated with nitric and perchloric acids to destroy the organic matter prior to their respective analyses. This wet-oxidation was imperative because sulfosalicylic acid interferes in the determination of these metals. The effluents were evaporated to a volume of about 30 ml. 10 ml. of concentrated nitric acid was added and the solutions were evaporated to 15 ml. 10 ml. nitric acid and 10 ml. concentrated perchloric acid were added and the solutions were evaporated to perchloric acid fumes. An additional 10 ml. of perchloric acid was added and the solutions were evaporated to near dryness. Using this procedure, hundreds of solutions were wet-oxidized with no hazardous explosions occurring. 2 ml. of concentrated sulfuric acid was added to the titanium solutions in order to effect their solution.

The mercury(II) effluents were titrated directly. The solutions containing iron(III) were evaporated to a convenient volume and analyzed directly by the photometric method.

Those metals which were eluted with hydrochloric or nitric acids were evaporated to near dryness to remove the excess acid prior to their titrimetric determination.

RESULTS AND DISCUSSION

The purpose of the ion exchange paper chromatography investigation of metal ions using sulfosalicylate eluant was to obtain a rapid qualitative relationship between the behavior of metals on ion exchange loaded paper and their behavior on conventional ion exchange resin. A preliminary study, using the data of Fritz and Umbreit (43), who used EDTA as an eluting agent, showed a good correlation between ion exchange paper and ion exchange resin.

R_f values (the distance moved by the metal ion divided by the distance moved by the eluant) were obtained as a function of pH. At low pH values the hydrogen ion competes favorably with metal ions for the carboxylate and the phenolate anions of sulfosalicylic acid. These anions are the coordination sites in the complexation of metal-sulfosalicylates. Therefore, in highly acidic solutions the metal complexes are largely dissociated, and both metal ions of a binary mixture are retained by the resin. In basic medium the metal complexes of low stability form neutral or anionic species. No separation is then possible as both metals pass quantitatively through the column. An intermediate pH range was determined which permits the proper equilibrium for quantitative separations.

The results of the measurement of the R_f values are in

Table 7. The failure of the qualitative tests for titanium and zirconium was due to the band smearing of the ions and the insensitivity of the qualitative tests used.

The results show that iron(III), uranium(VI), titanium(IV), zirconium(IV), thorium(IV), and possibly copper(II) may be eluted with sulfosalicylate from cation exchange resin. In the ion exchange paper study, only one column volume of eluant was added. However, in an actual column procedure up to ten column volumes of eluant are applied, thus assuring the complete elution of the metal complexes.

Besides the above data, a knowledge of the stability constants of the metal-sulfosalicylic acid (H_3SSA) complexes is helpful in the prediction of the elution behavior of metal ions on cation exchangers. However, much of the literature is contradictory and confusing in this respect.

Foley and Anderson (59, 60) have studied the iron-sulfosalicylate complex spectrophotometrically. They found that iron forms a 1:1 complex with sulfosalicylate up to pH 7.8. They postulated the possibility of iron(III)hydroxy complexes at high pH. Banks and Patterson (61) reported the 1:3 $Fe(SSA)_3^{-6}$ complex exists in neutral and alkaline solutions. Agren (62) has found potentiometrically and photometrically that 1:1 FeSSA, 1:2 $Fe(SSA)_2^{-3}$, and 1:3 $Fe(SSA)_3^{-6}$ iron-sulfosalicylate

Table 7. Determination of the R_f values for metal ions on cation exchange paper using sulfosalicylate eluant

Metal ion	pH	Range of R_f values	Average R_f
Fe(III)	5.0	0 -0.41	0.20
	6.0	0.13-0.45	0.29
U(VI)	5.0	0 -0.28	0.14
	6.0	0 -0.31	0.16
Ti(IV)	5.0	test fails	
	6.0	test fails	
Zr(IV)	5.0	test fails	
	6.0	test fails	
Co(II)	6.0	0	0
La(III)	7.0	0	0
Th(IV)	6.0	0 -0.44	0.22
Y(III)	6.0	0	0
	7.0	0	0
Cu(II)	5.0	0.03-0.09	0.06
	6.0	0.07-0.25	0.16
Hg(II)	6.0	0	0
	7.0	0	0
Zn(II)	7.0	0	0
Ni(II)	6.0	0	0
	7.0	0	0

complexes are formed at pH 2, 4, and 6 to 7, respectively. Perrin (63) reported the log stepwise stability constants of 14.60 and 10.55 for the 1 to 1 and 1 to 2 ironsulfosalicylate complexes.

Foley and Anderson (64) showed that only a 1:1 uranium(VI) sulfosalicylate complex exists in the pH range of 2 to 10. They state the maximum stability of this complex is at pH 4.7. However, Banks and Singh (65) found that $UO_2(SSA)_2^{-1}$ and $UO_2(SSA)_2^{-4}$ are formed at pH 4.5 and 7.5, respectively. The log stepwise stability constants of 11.14 and 8.06 are reported.

Aluminum(III) forms 1:1, 1:2, and 1:3 complexes with sulfosalicylate at pH values of 3.8, 5.5, and 8.5, respectively (65). The log k values by Bjerrum's method for the stepwise stability constants are 13.20, 9.63, and 6.06.

Turner and Anderson (66) determined spectrophotometrically that 1:1 and 1:2 copper(II)-sulfosalicylate complexes exist at pH 3 to 5.5 and pH greater than 8.5, respectively. Vasil'ev and Gorokhovskii (67) reported in the pH range of 3 to 6 1:1 and 1:2 Cu(II) sulfosalicylate complexes exist. Log stepwise constants of 9.50 and 6.80 have been reported for copper(II) (63). Ishibashi *et al.* (68) reported a 1:2 titanium(IV)-sulfosalicylate complex at pH 9.5.

Perrin (63) measured the stepwise stability constants for manganese(II), cobalt(II), nickel(II), zinc(II), and cadmium(II). The respective log k_1 values are 5.10, 6.00, 6.30, 6.05, and 4.65. The log k_2 values for Mn(II), Co(II), a and Ni(II) are 2.90, 3.60, and 3.90, respectively.

Using the stability constants reported by Perrin and the ionization constants for sulfosalicylic acid, the sulfosalicylate complexes of Mn(II), Co(II), Ni(II), Zn(II), and Cd(II) are largely dissociated at pH 6 and the metals should be retained by cation exchange resin. The log of the effective stability constant for the 1:1 metal sulfosalicylate complexes of Fe(III), Al(III), U(VI), and Cu(II) at pH 6 are 8.6, 6.2, 5.1, and 3.5, respectively.

The elution behavior of several individual metal ions was studied on Dowex 50W-X8, using the procedure employed in the separation of mixtures. The results are found in Table 8. The results show that iron(III), aluminum(III), titanium(IV) and vanadium(IV) are quantitatively eluted with sulfosalicylate at pH 6.0. Mercury(II) and thorium(IV) are incompletely eluted at pH 6 and 7, respectively. Cobalt(II) is retained by the ion exchange resin at pH 6.

These results compare favorably with the findings in the ion exchange paper investigation, except for the behavior of mercury(II) and thorium(IV). The anomalous results for

Table 8. Elution of metal ions as a function of pH

Metal ion	pH	Milligrams metal taken	found	Per cent eluted
Fe(III)	5.0	13.49	12.73	94.4
	5.0	13.49	13.28	98.4
	6.0	13.49	13.83	102.5
	6.0	13.49	13.59	100.6
Co(II)	6.0	14.70	0	0
	6.0	14.70	0	0
Al(III)	5.0	6.56	6.40	97.5
	5.0	6.56	6.37	97.1
	6.0	6.56	6.55	99.8
	6.0	6.56	6.58	100.2
Th(IV)	6.8	56.65	55.87	98.6
	7.0	56.65	55.98	98.8
Ti(IV)	5.0	11.11	11.16	100.4
	4.9	11.11	11.25	101.3
	6.0	11.11	11.18	100.7
	6.0	11.11	11.13	100.2
V(IV)	6.0	10.12	10.17	100.5
	6.0	10.12	10.15	100.2
	6.6	10.12	10.15	100.2
	6.5	10.12	10.12	100.0
Hg(II)	6.0	54.50	52.48	96.3
	6.0	54.50	52.21	95.8

mercury were due to the use of ammonium acetate buffer in the procedure for determining the R_f values on ion exchange paper. Mercury(II) forms ammine complexes in the presence of ammonia. A mercury compound probably precipitated on the paper, causing a zero for the R_f value. In the procedure for the separation of metal ions, ammonia was avoided to prevent metal-ammonia complexes. The incomplete elution of thorium was due to the extremely high resin affinity of tetravalent thorium which offsets the formation of the thorium sulfosalicylate complex.

Several binary mixtures containing iron(III) were separated. The results are reported in Table 9. The iron-mercury separation failed. However, the titrimetric analysis of iron yielded theoretical recovery.

Separations involving uranium(VI) are reported in Table 10. The recoveries of uranium were about one per cent low using pH 6 sulfosalicylate eluant. However, pH 6.5 eluant quantitatively separated uranium from many metal ions. The separation of uranium from lead was not possible at pH 6.5, owing to the precipitation of lead at this pH. An uranium-copper separation was accomplished. This was anomalous as subsequent copper separations from iron, aluminum, and titanium failed because copper was partially eluted with sulfosalicylate.

Table 9. Separation and analysis of iron(III)-metal ion mixtures

Separation of iron from metal 1	pH	Milligrams iron taken	found	diff.	Milligrams metal 1 taken	found	diff.
Fe(III)-Co(II)	6.1	14.47	14.68	+0.21	14.70	14.67	-0.03
	6.0	14.47	14.65	+0.18	14.70	14.76	+0.06
Fe(III)-Ni(II)	6.1	14.45	14.54	+0.09	14.44	14.35	-0.09
	6.1	14.45	14.48	+0.03	14.44	14.35	-0.09
Fe(III)-Zn(II)	6.1	14.45	14.45	0.00	16.44	16.50	+0.06
	6.1	14.45	14.48	+0.03	16.44	16.44	0.00
Fe(III)-Hg(II)	6.0	14.48	14.48	0.00	54.50	--	
	6.0	14.48	14.48	0.00	54.50	--	
Fe(III)-Mg(II)	6.1	14.45	14.48	+0.03	5.44	5.47	+0.03
	6.1	14.45	14.48	+0.03	5.44	5.45	+0.01
Fe(III)-La(III)	6.2	14.48	14.51	+0.03	28.47	28.47	0.00
	6.2	14.48	14.48	0.00	28.47	28.41	-0.06
Fe(III)-Cd(II)	6.1	14.51	14.54	+0.03	27.76	27.93	+0.17
	6.1	14.51	14.59	+0.08	27.76	27.87	+0.11
Fe(III)-Pb(II)	6.2	14.48	14.54	+0.06	49.43	49.53	+0.10
Fe(III)-Y(III)	6.3	14.54	14.59	+0.05	25.47	25.52	+0.05
	6.3	14.54	14.54	0.00	25.47	25.47	0.00
Fe(III)-Yb(III)	6.4	14.59	14.59	0.00	46.15	45.98	-0.17
	6.3	14.59	14.54	-0.05	46.15	46.15	0.00

Table 10. Separation and analysis of uranium(VI)-metal ion mixtures

Separation of uranium from metal 1	pH	Milligrams uranium			Milligrams metal 1		
		taken	found	diff.	taken	found	diff.
U(VI)-Cu(II)	6.2	60.18	59.79	-0.39	16.26	16.35	+0.09
	6.2	60.18	60.05	-0.13	16.26	16.38	+0.12
U(VI)-Ni(II)	6.1	60.12	59.79	-0.33	14.46	14.52	+0.06
	6.1	60.12	59.66	-0.46	14.46	14.49	+0.03
U(VI)-Cd(II)	6.7	60.52	60.07	-0.45	27.82	27.98	+0.16
	6.7	60.52	60.59	+0.07	27.82	27.98	+0.16
U(VI)-La(III)	6.1	60.52	60.37	-0.15	28.47	--	
	6.1	60.52	60.22	-0.30	28.47	--	
U(VI)-Mg(II)	6.7	60.89	60.74	-0.15	5.42	5.42	0.00
	6.7	60.89	60.74	-0.15	5.42	5.44	+0.02
U(VI)-Pb(II)	6.1	60.89	60.22	-0.67	49.53	49.74	+0.21
	6.1	60.89	60.37	-0.52	49.53	49.63	+0.10
U(VI)-Ni(II)	6.8	121.2	120.9	-0.3	2.90	3.10	+0.20
	6.8	121.2	120.9	-0.3	2.90	2.99	+0.09
U(VI)-Co(II)	6.9	121.5	121.6	+0.1	29.46	29.46	0.00
	6.9	121.5	121.9	+0.4	29.46	29.47	+0.01
	6.7	12.00	12.57	+0.57	29.52	29.43	-0.09
	6.7	12.00	12.30	+0.30	29.52	29.55	+0.03

The results of titanium(IV) separations are in Table 11. Slightly high recoveries of titanium were obtained. The error was in the method of analysis for titanium. Titanium "blanks" were prepared and were treated with the sulfosalicylate eluant and were wet-oxidized with nitric and perchloric acids. The blank determinations gave consistently one per cent high recoveries. The high concentration of chloride in the titanium(IV) solution caused the failure of a titanium-cadmium separation. A cadmium chloride complex was co-eluted with the titanium-sulfosalicylate complex.

Table 11. Separation and analysis of titanium(IV)-metal ion mixtures

Separation of titanium from metal 1	pH	Milligrams titanium			Milligrams metal 1		
		taken	found	diff.	taken	found	diff.
Ti(IV)-Co(II)	6.0	11.11	11.28	+0.17	14.70	14.73	+0.03
	6.0	11.11	11.25	+0.14	14.70	14.70	0.00
Ti(IV)-Ni(II)	6.0	11.11	11.25	+0.14	14.46	14.46	0.00
	6.0	11.11	11.25	+0.14	14.46	14.46	0.00
Ti(IV)-Mg(II)	6.0	11.11	11.20	+0.09	5.42	5.48	+0.06
	6.0	11.11	11.23	+0.12	5.42	5.49	+0.07

Results of the vanadium(IV) separations are in Table 12. Vanadium was successfully separated from cobalt, zinc, ytterbium, and magnesium.

The separations of aluminum from zinc, manganese, mag-

Table 12. Separation and analysis of vanadium(IV)-metal ion mixtures

Separation of vanadium from metal 1	pH	Milligrams vanadium			Milligrams metal 1		
		taken	found	diff.	taken	found	diff.
V(IV)-Co(II)	6.1	20.20	20.22	+0.02	29.49	29.49	0.00
V(IV)-Zn(II)	6.0	10.12	10.20	+0.08	16.02	16.31	+0.29
	6.0	10.12	10.15	+0.03	16.02	16.15	+0.13
	6.0	2.42	2.48	+0.06	32.77	32.87	+0.10
	6.0	2.42	2.48	+0.06	32.77	32.87	+0.10
V(IV)-Mg(II)	6.1	10.10	10.20	+0.10	5.42	5.53	+0.11
	6.1	10.10	10.22	+0.12	5.42	5.53	+0.11
	6.2	10.12	10.40	+0.28	46.23	46.32	+0.09

nesium, nickel, lead, cadmium, yttrium, ytterbium, and lanthanum are reported in Table 13. The aluminum-manganese separation was not quantitative, owing to the elution of some manganese with sulfosalicylate. Manganese probably was oxidized to trivalent manganese, forming a manganese(III)-sulfosalicylate complex of higher stability than the manganese(II)-sulfosalicylate complex. Diehl and Butler (69) found that manganese is quantitatively oxidized to manganese(III) in the presence of sulfosalicylate with potassium ferricyanide. The separation of aluminum and manganese was quantitative when the sample and the eluant contained ascorbic acid which prevented the oxidation of manganese.

Binary mixtures of ten to 1 molar ratio of aluminum to yttrium, magnesium, and zinc were separated. Aluminum as a minor constituent was successfully separated from zinc and magnesium on 4 cm. columns and from nickel and cadmium on 8 cm. columns.

Table 13. Separation and analysis of aluminum(III)-metal ion mixtures

Separation of aluminum from metal 1	pH	Milligrams aluminum			Milligrams metal 1		
		taken	found	diff.	Taken	found	diff.
Al(III)-Zn(II)	6.0	6.59	6.59	0.00	16.44	16.50	+0.06
	6.0	6.59	6.60	+0.01	16.44	16.44	0.00
	6.1	13.22	13.23	+0.01	3.20	3.26	+0.06
	6.1	13.22	13.22	0.00	3.20	3.23	+0.03
	6.0	1.38	1.39	+0.01	32.04	32.14	+0.10
	6.0	1.38	1.38	0.00	32.04	32.10	+0.06
Al(III)-Mn(II)	---	6.57	6.92	+0.35	14.22	13.57	-0.65
	---	6.57	6.94	+0.37	14.22	13.57	-0.65
Al(III)-Mn(II)[a]	6.1	6.59	6.63	+0.04	14.27	14.51	+0.24
	6.1	6.59	6.62	+0.03	14.27	14.51	+0.24
Al(III)-Mg(II)	6.0	6.58	6.59	+0.01	5.44	5.47	+0.03
	6.0	13.20	13.18	-0.02	1.08	1.13	+0.05
	6.0	13.20	13.18	-0.02	1.08	1.12	+0.04
	6.0	1.38	1.38	0.00	10.84	10.86	+0.02
	6.0	1.38	1.38	0.00	10.84	10.84	0.00

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[a] Ascorbic acid present

Table 13. (Continued)

Separation of aluminum from metal 1	pH	Milligrams aluminum taken	found	diff.	Milligrams metal 1 taken	found	diff.
Al(III)-Ni(II)	---	6.58	6.61	+0.03	14.46	14.55	+0.09
Al(III)-Ni(II)[b]	6.0	1.38	1.39	+0.01	29.08	29.11	+0.03
	6.1	1.38	1.42	+0.04	29.08	29.11	+0.03
Al(III)-Pb(II)	6.0	6.59	6.62	+0.03	49.43	48.10	-1.33
	6.0	6.59	6.65	+0.06	49.43	50.25	+0.82
Al(III)-Cd(II)	6.0	6.59	6.61	+0.02	27.70	27.87	+0.17
	6.0	6.59	6.62	+0.03	27.70	27.76	+0.06
Al(III)-Cd(II)[b]	6.0	1.39	1.39	0.00	55.37	--	
	6.0	1.39	1.39	0.00	55.37	--	
Al(III)-Y(III)	6.2	6.59	6.63	+0.04	25.47	25.47	0.00
	6.3	6.59	6.63	+0.04	25.47	25.47	0.00
	6.0	13.20	13.18	-0.02	5.05	5.05	0.00
	6.0	13.20	13.18	-0.02	5.05	5.01	-0.04
Al(III)-Yb(III)	6.3	6.61	6.66	+0.05	46.15	45.72	-0.43
	6.3	6.61	6.65	+0.04	46.15	45.89	-0.26
Al(III)-La(III)	6.1	6.59	6.65	+0.06	28.47	28.47	0.00
	6.1	6.59	6.65	+0.06	28.47	28.41	-0.06

[b] 8 cm. column

The separation of 1:10 molar ratio of aluminum to yttrium was investigated. This separation failed on 4 and 8 cm. columns, using 0.05 M acetate as the eluant. Using 0.10 M acetate eluant to control the pH better, this separation was successful on ion exchange columns of 4 or 8 cm. length. Yttrium(III) forms a weak sulfosalicylate complex which was partially eluted above pH 6.5, while below pH 6.2 yttrium was quantitatively adsorbed on the resin. Table 14 presents the results.

Table 14. Separation and analysis of 1:10 molar ratio of aluminum(III)-yttrium(III) mixtures

Length of column	Molarity of buffer	pH	Milligrams aluminum			Milligrams yttrium		
			taken	found	diff.	taken	found	diff.
4 cm.	0.05 M	6.6	1.38	2.15	+0.77	51.17	48.44	-2.73
8	0.05	6.5	1.39	1.75	+0.36	51.25	49.69	-1.56
8	0.05	6.5	1.39	1.83	+0.44	51.25	49.69	-1.56
4	0.10	6.2	1.38	1.37	-0.01	51.24	51.19	-0.05
4	0.10	6.2	1.38	1.43	+0.05	51.24	51.10	-0.14
8	0.10	6.2	1.38	1.39	+0.01	51.24	51.19	-0.05
8	0.10	6.2	1.38	1.38	0.00	51.24	51.24	0.00

Separations of zirconium from cobalt and zinc are reported in Table 15.

Table 15. Separation and analysis of zirconium(IV)-metal ion mixtures

Separation of zirconium from metal 1	pH	Milligrams zirconium			Milligrams metal 1		
		taken	found	diff.	taken	found	diff.
Zr(IV)-Co(II)	6.0	27.25	----		14.78	14.81	+0.03
	6.0	27.25	----		14.78	14.78	0.00
Zr(IV)-Zn(II)	6.1	27.25	27.03	-0.22	16.40	16.47	+0.07
	6.1	27.25	27.10	-0.15	16.40	16.43	+0.03

The separations were rapid and generally quantitative. The metal ion which forms sulfosalicylate complexes was collected in the first 60-ml. of eluate, while the adsorbed cation was retained at the top of the resin bed as a narrow band. The pH of the sample as it passed through the column was maintained using acetate buffers as dilute as 0.05 M.

The average recovery for the successful separations is 100.5 per cent with an average deviation of 0.4 per cent. The bias toward high results is due to two reasons. Those samples which were wet-oxidized with nitric and perchloric acids usually gave high results. Parallel blank determinations gave similarly high recoveries.

The solutions containing the metals eluted with acid contained large amounts of sodium salts. In the presence of this high concentration of salts, the end point reactions in the titrimetric analyses are sluggish. It was found that by titrating slowly close to the end points nearly theoretical recoveries were obtained.

SUMMARY

The elution behavior of metal ions in the presence of sulfosalicylate was studied on cation exchange paper. R_f values for the metal ions were obtained as a function of pH. From these data pH conditions for the quantitative separation of binary mixtures on Dowex 50W-X8 were determined.

Using pH 6 sulfosalicylate eluant, iron(III), aluminum(III) titanium(IV), vanadium(IV), and zirconium(IV) are quantitatively eluted from the resin. Under this condition cadmium(II), zinc(II), cobalt(II), lead(II), nickel(II), yttrium(III), ytterbium(III), lanthanum(III), manganese(II), and magnesium(II) are retained by the resin. pH 6.5 sulfosalicylate elutes uranium(VI). Copper(II) and mercury(II) are incompletely eluted with sulfosalicylate at pH 6. Thorium(IV) is not quantitatively eluted with pH 7 sulfosalicylate.

Many binary mixtures were resolved on 4 and 8 cm. columns with generally good precision and accuracy. Samples varied from 0.05 to 0.5 millimole of each metal ion in the mixture.

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