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The Radiochemistry
of Sulfur

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COMMITTEE ON NUCLEAR SCIENCE

The Radiochemistry of Sulfur

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Subcommittee on Radiochemistry
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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

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INTRODUCTION

This volume which deals with the radiochemistry of sulfur is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of sulfur which might be included in a revised version of the monograph.

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Remy, H., Treatise on Inorganic Chemistry, Volume I, p. 698-741, Elsevier, Amsterdam, 1956.

Kleinberg, J., Argersinger, W. J., Jr., and Griswold, E., Inorganic Chemistry, p. 434-455, Heath, Boston (1960).

Fairlie, A. M., Sulfuric Acid Manufacture, Reinhold, New York, (1936).

Latimer, W. M., and Hildebrand, J. H., Reference Book of Inorganic Chemistry, 3rd Edition, MacMillan, New York (1951).

II. RADIOACTIVE NUCLIDES OF SULFUR

The radioactive nuclides of sulfur that are of interest in the radiochemistry of sulfur are given in Table I. This Table has been compiled from information appearing in reports by Strominger, et al,[1] and by Hughes and Harvey.[2]

TABLE I

THE RADIOACTIVE NUCLIDES OF SULFUR

Radio-Nuclide	Half-life	Mode of Decay	Energy of Radiation, Mev	Produced By
S^{31}	3.2 s	β^+	β^+ 4.1	Si-α-n, P-p-n, S-γ-n
S^{35}	8 d	β^-	β^- 0.167	S-n-γ, S-d-p, Cl-n-p Cl-d-α
S^{37}	5.04 m	β^-	β^- 1.60, 4.7 γ 3.1	S-n-γ, Cl-n-p
S^{38}	2.87 h	β^-	β^- 1.1, 3.0 γ 1.88	S^{36}-t-p

III. REVIEW OF THE CHEMISTRY OF SULFUR

Sulfur composes about 0.05 percent of the earth's crust and exists mainly in the free state and as either sulfides or sulfates. The most abundant metal sulfides are pyrite, FeS_2, chalcopyrite, $CuFeS_2$, galena, PbS, and zinc blende, ZnS. The more important sulfate compounds are gypsum, $CaSO_4 \cdot 2H_2O$, epsom salt and kieserite, $MgSO_4$, barytes, $BaSO_4$, celestine, $SrSO_4$, and glauberite, Na_2SO_4.

Elemental sulfur is chiefly obtained by an extraction process which consists of melting and subliming it from the materials that contain it in the elementary state.[3]

1. Elemental Sulfur

Sulfur can exist in several modifications and many investigations have been carried out in an attempt to explain the various forms of sulfur. A very excellent general report on these investigations and the properties of sulfur can be obtained from Remy.[3]

The stable form of sulfur at ordinary temperature is rhombic sulfur. It is yellow in color and its electrical and thermal conductivities are extremely small. It will not dissolve in water and it is partially soluble in benzene, alcohol, ether, and other organic solvents. It is soluble in carbon disulfide, and as the solution stands, the sulfur will recrystallize. At temperatures above 110°, rhombic sulfur will melt to form a yellow, mobile liquid. Following a process of partial solidification in which the liquid sulfur is poured off, the residue is found to be composed of almost colorless, needle-shaped crystals of the monoclinic form of sulfur. This form of sulfur is unstable and after a time will be transformed to rhombic sulfur. Another modification, also monoclinic, can be obtained in the form of yellow-white leaflets by rapidly cooling saturated solutions of sulfur in benzene, turpentine, or alcohol or by allowing ammonium polysulfide solutions to stand in air. This modification is unstable at all temperatures.

Molten sulfur when strongly heated undergoes a number of physical changes. At temperatures above 160°, it is brown in color and its viscosity increases as the temperature rises. When heated above 200°, it is dark brown and has a resinous viscosity. This viscosity diminishes when the tem-

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perature is raised to 250°, and it becomes a mobile liquid at 400°. Sulfur

boils at a temperature of 444.6°.

2. Compounds of Sulfur

Sulfur is a very reactive element, and it remains quite reactive even

at elevated temperatures. It can form compounds having oxidation states of

-2 (the sulfides), +2 (the thiosulfates and pentathionates), +3 (the hypo-

sulfites), +4 (the sulfites), +5 (the dithionates), and +6 (the sulfates).[4]

Sulfur also exhibits an oxidation state of +1 (as well as +2, +4, +5, and +6)

with the halogens.

In most of its reactions with the elements, sulfur resembles oxygen. It

will combine directly with almost all of the elements, and it exhibits a

strong exothermic reaction in its combination with the metals. In a notable

exception to its resemblence to oxygen, sulfur will combine directly with all

of the halogens, except iodine. It will burn in air to produce dioxides but

Table II. Solubility of Sulfur Compounds

Compound	Formula	Water Solubility		Other Solvents
		Cold	Hot	
Bromide	S_2Br_2	Decomposes	Decomposes	Soluble in CS_2
Chlorides	S_2Cl_2	Decomposes	Decomposes	Soluble in CS_2, ether and benzene
	SCl_2	Decomposes	Decomposes	Decomposes in alcohol and ether; soluble in benzene and CCl_4
	SCl_4	Decomposes	Decomposes	
Fluorides	S_2F_2	Decomposes	Decomposes	Decomposes on KOH
	SF_4	Decomposes	Decomposes	
	S_2F_{10}			Decomposes in Fused caustic
	SF_6	Very slightly soluble	Slightly soluble	Soluble in KOH; slightly soluble in alcohol
Nitrides	S_4N_2	Insoluble		Soluble in Ether; slightly soluble in alcohol and CS_2
	S_4N_4	Decomposes		Soluble in CS_2, benzene chloroform, NH_3; slightly soluble in alcohol and ether
Oxides	SO	Decomposes		
	S_2O_3	Decomposes	Decomposes	Soluble in fuming H_2SO_4
	SO_2	22.8	0.58^{90}	Soluble in alcohol, H_2SO_4 and acetic acid
	SO_3	Decomposes	Decomposes	Firms fuming H_2SO_4
	$(SO_3)_2$	Decomposes	Decomposes	
	S_2O_7	Decomposes	Decomposes	Soluble in H_2SO_4
	SO_4	Soluble decomposes		Decomposes in dilute H_2SO_4
Oxy-Salts	S_2OCl_4	Decomposes	Decomposes	Decomposes violently with alcohol
	$S_2O_3Cl_4$	Decomposes	Decomposes	Decomposes in alcohol

will not combine directly with nitrogen. It will form homopolyatomic anions by direct combination with the appropriate anion. Sulfur will dissolve in concentrated nitric acid and will react with concentrated alkali solutions.

Table II lists many of the sulfur compounds and gives general information on the solubility of each of the compounds tabulated. More specific information on the reactions of sulfur and its compound formations follows:

a. Oxide, Oxyacid, and Oxyhalide Compounds of Sulfur. Sulfur can combine with oxygen to form the binary compounds of sulfur dioxide, SO_2, and sulfur trioxide, SO_3. Other normal oxides of sulfur are disulfur trioxide, S_2O_3, and sulfur monoxide, SO. Two peroxides, sulfur heptoxide, S_2O_7, and sulfur tetroxide, SO_4, can also be formed by reactions involving sulfur and oxygen.

Sulfur dioxide, SO_2, can also be formed either by burning sulfur in air or by heating sulfides in air or oxygen, or by reducing hot concentrated sulfuric acid with copper, mercury, carbon, or sulfur. SO_2 is a pungent smelling gas that will not burn or support combustion. It is very soluble in water (70 volumes of SO_2 can be dissolved in 1 volume of water at $0°$). When dissolved in water, the aqueous solution has a distinct acid reaction in that it contains the dibasic acid, H_2SO_3, or sulfurous acid. H_2SO_3 does not exist in the free state because it readily breaks up into sulfur dioxide and water. Thus, SO_2 is the anhydride of sulfurous acid. The salts derived from H_2SO_3 are the acid sulfites, M^1HSO_3, and the normal sulfites, $M_2^1SO_4$. The sulfites are usually prepared either by dissolving the corresponding metal in aqueous H_2SO_3 or by saturating solutions of metallic hydroxides or carbonates with sulfur dioxide.

The acid sulfites (or bisulfites) can be decomposed by strong acids; SO_2 gas is liberated during this process. They are very soluble in water. The normal sulfites also can be decomposed by a strong acid to liberate SO_2. All of the normal sulfites, except the alkali and ammonium sulfites, are only slightly soluble in water but will dissolve completely in aqueous H_2SO_3. The sulfite compounds can be easily oxidized in an oxygen atmosphere to sulfates; thiosulfates $M_2S_2O_3$, can be prepared by adding powdered sulfur to boiling alkali sulfite solutions. The sulfites can easily be reduced to dithionites,

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$M_2S_2O_4$, by adding zinc dust to their solutions. If dry sulfite salts are heated in the presence of carbon, zinc, or other metals, they are reduced to sulfides. If the dry salts are reacted with phosphorous oxychloride, thionyl chloride, $SOCl_2$, is formed. Bivalent heavy metal sulfites have a tendency to form complex compounds, such as the sulfito-salts.

Thiosulfates of the alkali metals, e.g., $Na_2S_2O_3$, can also be formed by the action of iodine on mixed solutions of the alkali sulfides and alkali sulfites. $Na_2S_2O_3$, which finds much use in analytical determinations by iodometry, can also be easily formed by the oxidation of sodium polysulfide, Na_2S_5, in an oxygen atmosphere. All of the thiosulfates, except those of lead, silver, thallium (I), and barium, are very soluble in water. The heavy metal thiosulfates will form trithiosulfato complex ions, e.g., $[Ag(S_2O_3)_3]^{5-}$, when they are dissolved in sodium thiosulfate solutions. The thiosulfates are decomposed by acids with the evolution of SO_2 and the deposition of free sulfur. If the reaction occurs in an aqueous solution, the deposition of sulfur is slow and it is assumed that thiosulfuric acid, $H_2S_2O_3$, is first formed. Since $H_2S_2O_3$ is highly unstable, it will exist for only a short time and ultimately SO_2 will be evolved and sulfur deposited. $H_2S_2O_3$ has never been isolated, but it is possible to prepare neutral thiosulfate salts by replacing the hydrogen atoms of the acid with metal ions.

Sulfur trioxide, SO_3, evolved as part of the gaseous mixture obtained by roasting pyrite or other sulfide ores, is formed when the gas is passed over a heated catalyst, such as vanadium oxide, and becomes the base material for the production of sulfuric acid, H_2SO_4. Small amounts of SO_3 can be prepared by heating either fuming sulfuric acid, or sodium pyrosulfate, $Na_2S_2O_7$, or other pyrosulfates and collecting it in a suitable container. SO_3 will condense on cooling into a colorless, transparent mass which fumes in air. Sulfur trioxide melts at 16.9° and boils at 44.8°. It absorbs water rapidly, combining with it to form sulfuric acid, H_2SO_4. Explosive reactions can occur when water is allowed to drop on to sulfur trioxide since SO_3 can abstract constitutively bound water from many substances; e.g., it

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has the ability to char organic materials such as cellulose.

Sulfuric acid is manufactured industrially by the Contact Process.[5] This process furnishes not only 98% sulfuric acid (sp. g. 1.841) but also fuming sulfuric acid (oleum). Fuming sulfuric acid contains an excess of dissolved sulfur trioxide. Pure concentrated H_2SO_4 is a colorless, oily, viscous liquid. It has a great affinity for water. Extreme caution must be excerised when diluting H_2SO_4 with water because a considerable amount of heat (20.42 kcal. per mol of H_2SO_4 at 20°) is liberated. Thus, sulfuric acid must always be poured into water in small amounts; water should never be poured into sulfuric acid. H_2SO_4 can absorb water vapor from the air, and it is frequently used as a drying agent. It can be used as a dehydrating agent in chemical reactions. It will char many organic compounds by abstracting water from them. When heated it will undergo an oxidizing action to be converted into sulfurous acid, H_2SO_3. Metals and other elements, such as carbon, are readily oxidized by concentrated H_2SO_4 and sulfur dioxide is liberated during the oxidation process. Dilute sulfuric acid will only dissolve those metals above hydrogen in the electromotive series. Fuming sulfuric acid is a much better dehydrating and oxidizing agent than sulfuric acid.

Sulfuric acid is a dibasic strong acid, and the salts derived from it are the acid, or hydrogen, sulfates, $MHSO_4$, and the normal, or neutral, sulfates, M_2SO_4. Sulfates may be prepared in a number of ways,[6] i.e., (1) by dissolving metals in H_2SO_4; (2) by neutralizing H_2SO_4 with metal oxides or hydroxides; (3) by decomposing the salts of volatile acids with H_2SO_4; (4) by double decomposition between a sulfate and a salt of the metal from which the sulfate is required; and (5) by the oxidation of sulfites or sulfides. The alkali metals are the only elements that form acid sulfates. These salts are produced either as a result of a crystallization process from normal sulfate solutions treated with excess H_2SO_4, or by decomposing the alkali salts of other acids with sulfuric acid at a moderately high temperature. The acid sulfates are water soluble. They can be fused and when heated above their melting points will form pyrosulfates, $M_2S_2O_7$. At higher temperatures, the pyrosulfates will decompose into normal sulfates and SO_3. The normal

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sulfates, except those for the alkaline earths, lead, and silver, are very soluble in water and can form crystalline hydrate compounds when the water is removed. The normal sulfates also form double, or sulfato, salts; polysulfates, $M_2S_3O_{10}$, can be produced by treating normal sulfates with sulfur trioxide.

Disulfur trioxide, S_2O_3, a blue crystalline crust, can be formed by the action of sulfur on completely anhydrous sulfur trioxide. S_2O_3 will dissolve only in fuming sulfuric acid and although its composition suggests that it is the anhydride of dithionous acid, $H_2S_2O_4$, no chemical relationship with this acid or its salts has yet been established.[7] Sulfur monoxide, SO, is a colorless gas and is formed by the action of a glow discharge on SO_2.[7] It will not react with oxygen at ordinary temperatures but will produce hydrogen sulfide, H_2S, and sulfurous acid, H_2SO_3, when it is reacted with water.

Sulfur heptoxide, S_2O_7, can be obtained by the action of an electric discharge on a sulfur dioxide-oxygen mixture.[8] It is formed as oily drops, which solidify at 0°. It can be decomposed with the evolution of oxygen in the presence of water. If the evolution of oxygen is prevented, the hydrolysis of the compound will give peroxydisulfuric acid. Sulfur tetroxide, SO_4, is also obtained as a white solid by the action of the electric discharge on a SO_2-O_2 mixture.[8] It can be dissolved in anhydrous sulfuric acid; it decomposes in water, giving off oxygen. SO_4 is a strong oxidizing agent and can be used to convert manganese (II) salts to permanganates and cuprates (II) to cuprates (III). SO_4 does not have the characteristics of an acid anhydride.[9] Two peroxyacids are derived from S_2O_7. These peroxyacids, peroxymonosulfuric acid, H_2SO_5, and peroxydisulfuric acid, $H_2S_2O_8$, are hydrogen peroxide derivatives of sulfuric acid, H_2SO_4.[10]

In addition to the peroxyacids and thiosulfuric acid, $H_2S_2O_3$, several other oxyacids and oxyacid salts of sulfur are known.[11] No known sulfur oxide compounds are known that correspond to the anhydrides of these acids. These other oxy acids can be categorized as being polythionic acid, $H_2S_xO_6$, (where x = 3, 4, 5, or 6) and dithionic acid, $H_2S_2O_6$. The respective salts of these acids are the polythionates, dithionates, dithionites (or hyposulfites) and sulfoxylates. Of these salts, $Na_2S_2O_4$, sodium dithionite, is

probably the most used in a laboratory; it is used as an absorbent for oxygen in gas analysis.

Sulfur can form oxyhalide compounds of the types SOX_2 and SO_2X_2. Known respectively as the _thionyl halides_, or sulfur (IV) oxyhalides, SOX_2, they are usually prepared by halogen exchange reactions with sulfur dioxide, e.g., the reaction between phosphorus and SO_2 to produce $SOCl_2$. The _sulfuryl halides_, or sulfur (VI) oxyhalides, SO_2X_2, are prepared in a number of ways. SO_2F_2, _sulfuryl fluoride_, is obtained by the decomposition of barium fluorosulfonate, $Ba(SO_3F)_2$; SO_2Cl_2, _sulfuryl chloride_, is prepared by the direct combination of SO_2 and chlorine in the presence of a catalyst; SO_2FCl, a mixed halide, is formed by the halogen exchange reaction between SO_2Cl_2 and antimony fluoride, SbF_3.

Thionyl halides are more reactive than the selenyl halide compounds of selenium. They are thermally unstable and when heated will decompose to yield SO_2, free halogen, and a lower halide, e.g., S_2Cl_2. They can be hydrolyzed by water to form SO_2, or sulfurous acid, and the halogen acid, e.g., HCl. _Sulfuryl_ halides exhibit varied characteristics. SO_2F_2 is less reactive than SOF_2. It will not react with water but is attacked by strong bases. The hydroxide ions react slowly to form fluoride and _fluosulfonate_ ions. Ammonia will decompose sulfuryl compounds to give _sulfamide_, $SO_2(NH_2)_2$, and related compounds. _Sulfuryl chloride_, SO_2Cl_2, is less stable than SO_2F_2; it can be completely hydrolyzed to give H_2SO_4 and HCl. _Thionyl_ and _sulfuryl_ compounds of iodine and _sulfuryl_ compounds of bromine have not as yet been characterized.

b. _Halogen Compounds of Sulfur_. Sulfur can be combined directly with fluorine to form the compounds S_2F_2, SF_2, SF_4, S_2F_{10}, and SF_6,[12] and with chlorine the compounds S_2Cl_2, SCl_2, and SCl_4. It will form only one compound of bromine, S_2Br_2, which is very unstable. No iodine compounds of sulfur have ever been isolated.

Sulfur monochloride, S_2Cl_2, is an orange colored liquid and when heated above 300°, will decompose into S_2 and Cl_2 and will be decomposed by water to form free sulfur, H_2S, sulfite and thiosulfate ions. _Sulfur dichloride_, SCl_2, is a solid and can be readily hydrolyzed with water to form sulfur, H_2S, sulfite

and thiosulfate ions. <u>Sulfur hexafluoride</u>, SF_6, shows that sulfur can be hexavalent. It is a colorless, odorless gas that is more soluble in alcohol than in water. It will not burn but can be decomposed by hydrogen sulfide when heated. <u>Disulfur decafluoride</u>, S_2F_{10}, is obtained as a by-product when SF_6 is prepared. It has the same chemical properties as SF_6. All of the known <u>tetrahalide</u> compounds, i.e., SF_4, SCl_4, are thermally unstable. They will react with water to give SO_2, or H_2SO_3, and the halide acids.

c. Miscellaneous Reactions of Sulfur

1. <u>Hydrogen Sulfide</u>. Sulfur can react directly with hydrogen to produce hydrogen sulfide, H_2S. However, since the yield of this reaction is very poor, hydrogen sulfide is generally prepared by the action of acids on metal sulfides, such as FeS, or by the hydrolysis of more reactive metal sulfides, particularly Al_2S_3.

Hydrogen sulfide is a colorless gas which can be condensed to a color-less liquid at $-60.4°$. It is a very toxic gas and rigid precautions must be followed as it is being used. H_2S is moderately soluble in water, and its aqueous solutions are slightly acid. It is a strong reducing agent, and it will react with HNO_3 to produce sulfur. It also reacts with SO_2, in the presence of moisture, to produce free sulfur. It can burn readily in air or oxygen to form SO_2.

H_2S will react with the more active metals, such as sodium, to produce sulfides. It also reacts readily with other metals in either acid or alkaline solution to produce metallic sulfides that are only sparingly soluble. This particular characteristic makes H_2S a useable reagent in most qualitative analysis methods.

2. <u>Carbon Disulfide</u>. Sulfur can react with red hot carbon to produce carbon disulfide, CS_2. Carbon disulfide is a colorless liquid. It will volatilize at $46°$ and freeze at $-112°$. CS_2 is highly inflammable, burning readily in air.

It is immiscible with water at room temperature, but it readily reacts with steam at $400°$. CS_2 will not react with the halogens at low temperatures; at high temperatures, the reactions can be vigorous and a variety of products

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produced. Alkalis will slowly attack it to produce H_2S and alkali metal carbonates.

3. _Sulfur Tetranitride_. Sulfur and nitrogen will not react directly; however, the binary sulfur nitrogen compound, _sulfur tetranitride_, N_4S_4, can be readily formed by passing ammonia into a solution of sulfur monochloride in benzene.[13] N_4S_4 is a yellow solid at room temperature, and it will melt at 178°. It is not very soluble in water and hydrolyzes very slowly when brought into contact with water. Rapid hydrolysis occurs when it is heated with alkali solutions. N_4S_4 reacts with the halogens to form compounds in which sulfur has a higher oxidation state, e.g., $S_4N_4Cl_4$.

IV. THE ANALYTICAL CHEMISTRY OF SULFUR

Many analyses for sulfur are usually completed by gravimetric precipitations either of the sulfide, sulfite, sulfate, or thiosulfate ions or as free sulfur.[14] The sulfide ions may be determined either as silver sulfide, arsenic (III) sulfide, lead sulfide, mercuric sulfide, or cupric sulfide.[15] The sulfite precipitations almost always are completed by oxidizing the sulfite ions to sulfate ions and precipitating as barium sulfate and weighing;[14] however, calcium sulfite can be precipitated quantitatively from an aqueous-alcoholic solution.[16,17] The sulfate ions may be determined as barium sulfate,[18] sodium sulfate,[19] ammonium sulfate,[20] hexamminocobalt (III) bromide sulfate,[21] or benzidine sulfate.[22,23] Also, strychnine chloride has been used to precipitate the peroxydisulfate compound, $C_{21}H_{22}O_2N_2 \cdot H_2SO_4$.[24] The thiosulfate ions may be decomposed and the free sulfur collected and weighed.[15,25] The thiosulfate ions may also either be heated with $Hg(CN)_2$ and the sulfur precipitated as HgS[26] or treated with silver nitrate to produce silver sulfide.[25,27] Sulfur may also be determined as free sulfur following an extraction with carbon disulfide.[28]

The gravimetric method of precipitating the sulfate ions with a 5% solution of barium chloride is the method most frequently used.[29] However, several investigations[30-35] concerned with the conditions of precipitating $BaSO_4$ and its properties have shown that this gravimetric method is not an

exact method for determining sulfur. For example, the precipitate is most frequently impure because of its adsorption of such impurities as nitrates, fluosilicates, selenates, fluorides, chromates, molybdates, and tungstates. Also, the presence of large amounts of Cr^{+6} ions can complex the sulfate sufficiently to prevent complete precipitation of $BaSO_4$. In addition, the barium sulfate also shows varied degrees of solubility depending upon the acidity of the solution used for the precipitating conditions.

The ease with which sulfur is separated from other elements is dependent upon the form in which it occurs, i.e., sulfate, sulfide, thiosulfate, etc. Iron, chromium, nickel, magnesium, barium, strontium, lead, copper, molybdenum, and the other elements of the hydrogen sulfide group are the chief interfering elements. The following information generally describes separation methods that have been used in separating and isolating sulfur from such elements as these before its gravimetric precipitation as one of the forms given above.

1. Separations By Precipitation

The interferences - chromates, molybdates, tungstates, selenates, fluosilicates, and fluorides - usually encountered in the $BaSO_4$ precipitation method[14] can be removed in a number of ways.[30-35] For example, the Cr^{+6} ions can be reduced with zinc and an acetate solution added to complex the Cr^{+3} ions; selenates can be reduced by boiling the precipitate in concentrated hydrochloric acid, and fluosilicate ions can be removed by boiling in an ammonical solution. Fluoride ions can be complexed with boric acid. A precipitation of $BaSO_4$ in the presence of ethylenediamine-tetracetic acid also assists in eliminating most of these interferences.[36] Iron and other elements can be separated from sulfate ions by a double precipitation with ammonium hydroxide from a hydrochloric acid solution.[29,36] Molybdenum can also be separated in a similar manner.[37] Magnesium and the alkaline earths can be separated by a fusion with sodium carbonate and extracting the melt with water.[29] The elements of the hydrogen sulfide group can be removed by saturating a dilute hydrochloric acid solution with H_2S.[29]

If the sulfur appears as sulfide ions, separations can be made by attacking the sample material with a strong acid to liberate H_2S.[38] The hydrogen sulfide can be trapped in zinc or cadmium acetate and precipitated either as zinc or cadmium sulfide. This method is selective for releasing sulfide ions from numerous anions. The low-solubility sulfides can be either oxidized to sulfate ions by hot concentrated HNO_3, or by boiling concentrated $HClO_4$, or by fusions with Na_2O_2 or Na_2CO_3-$NaNO_3$.[39] Soluble sulfides can be oxidized by hydrogen peroxide in ammonical solution.[39] The sulfides can also be oxidized by heating in a stream of oxygen or air and the liberated SO_2 collected in hydrogen peroxide.[40] Usually the sulfate ions obtained from these oxidations are determined gravimetrically by a precipitation as $BaSO_4$. Similar techniques have been used in determining sulfur as the sulfite ions[41,42] or as the thiosulfate ions.[39]

2. Separations By Volatility

Sulfur, contained in steels and similar materials usually as sulfide ions, is most often determined by an evolution method in which a treatment of the sample material with acid and heating will liberate hydrogen sulfide.[29,43] The H_2S is adsorbed in ammoniacal solution of cadmium chloride and then oxidized to sulfate ions. Sulfur contained as sulfate ions in metals have also been determined by a system involving the volatility of hydrogen sulfide.[44] The metal was dissolved in HCl-HNO_3 and the sulfate ions reduced to sulfide ions with HI⁻ and distilled as H_2S. Of some concern in these investigations have been the partial oxidation of hydrogen sulfide by either higher oxides or some physical phenomena.[29] In one study[45] stannous chloride has been used in the sample dissolution method to prevent the oxidation of hydrogen sulfide.

A reducing mixture of phosphoric acid and 10-20% $SnCl_2 \cdot 2H_2O$ has also been used in a hydrogen sulfide evolution method to determine sulfur as a methylene blue complex.[46,47] This particular technique has been extended to the determination of S^{35} (88 d) either for radioactivity measurements or as part of an investigation of sulfur-35 in neutron-irradiated metals, soils, water, and biological materials.[48] Selenium, the halogens, and the hydrogen

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compounds of other elements that boil below 300° C can interfere in analyses by these techniques.

3. Separations By Electrolysis

Sulfur can not be electrolytically deposited on a cathode; However, an electrolysis of a dilute acid solution by means of a mercury cathode has been used to collect and separate iron, copper, chromium, molybdenum, and nickel from sulfur prior to its precipitation as barium sulfate.[49] The electrolysis was carried out at 0.8 to 1.0 ampere for 5 to 6 hours.

4. Separations By Solvent Extraction

No direct solvent extraction methods appear to exist for the determination of sulfur in any of its forms. However, a mixture containing 90 parts of ethyl alcohol, 10 parts of methyl alcohol, and 1 part of H_2SO_4 has been used to separate $MgSO_4$ from $CaSO_4$.[50] More than 0.46 gram of $MgSO_4$, but less than 0.1 gram of $CaSO_4$, is soluble in this system. Similarly, a very efficient and simple extraction of neutron-irradiated ferric chloride dissolved in concentrated HCl with isopropyl ether has been used by Wilk[51] to produce carrier-free S^{35} tracer.

5. Chromatographic Separations

a. By Inorganic Adsorbents. A chromatographic separation involving an alumina column has been used to determine sulfur in iron and steel.[52] The column retains the sulfuric acid while all the interferring ions pass through the column or are removed by washing, after which the sulfuric acid is isolated and determined.

b. By Ion Exchange Resins. The anion exchange resin, Amberlite IRA-400, in the chloride form and elutions with 0.1 M HCl have been used by several investigators to separate radioactive S^{35} (88 d) as a carrier-free species from neutron-irradiated KCl.[53-56] Cation exchangers have been used to separate sulfate ions from accompanying cations.[57,58]

c. By Paper Chromatography. The movement rate of SO_4^{--} ions on a paper chromatogram has been studied using solvents containing butanol-HCl[59] or butanol-pyridine-NH_4OH;[60] whereas, sulfide ions have been investigated using either n-butanol-ethanol-water mixture[61] or butanol-NH_4OH.[62] Sulfites,[60] thiosulfates,[62] and polythionates[63] have also been

separated by paper chromatographic techniques. Sulfates have been separated from phosphates by use of butanol-N-HCl solvents. [64] Sulfur-35 has also been determined in neutron-irradiated compounds by a paper chromatography method. [65]

V. DISSOLUTION OF SAMPLES CONTAINING SULFUR

Many different methods have been used to decompose materials containing sulfur because of the form in which the sulfur is present in the material. [29] For example, metals and alloys are usually put into solution by acid mixtures. One special procedure used in analyzing sulfur in steel consists of the ignition of the steel in an oxygen atmosphere at temperatures above 1400° and absorbing the sulfur oxides in hydrogen peroxide. [40] Ores, consisting mainly of sulfides, can be decomposed by a mixture of 3 parts of HNO_3 and 1 part of HCl. [14,66] Fuming nitric acid and heating in a sealed tube to 125° has also been used to decompose sulfide-containing materials. [67] Sodium peroxide fusions [68] and fusions with sodium carbonate and sodium nitrate have also been used to decompose ores and minerals. Combustions in a Parr bomb in the presence of sodium peroxide are used to destroy organic materials for a sulfur determination. [69]

Any one of these methods can be adapted for use in a radiochemical method for radiosulfur. The addition of sulfur carrier to the mixture before a decomposition is made will assist in the exchange of the various sulfur species in the sample material being analyzed.

VI. SAFETY PRACTICES

Most chemical species exhibit some degree of toxicity. Pieters and Creyghton's manual [70] is one of several recent manuals that report on the safe-handling of nonradioactive elemental compounds. Such a manual as this should be consulted before any analysis is undertaken. Once a material has been made radioactive, then the importance of safe-handling practices is increased. Any discharge of radioactivity into a laboratory area by explosion or spilling can be hazardous to personnel and can result in widespread contamination. Many sources of information exist on practices to be followed in processing radioactive materials

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and should be consulted. Typical of these are the safety procedures given in the Oak Ridge National Laboratory[71] and in the International Atomic Energy Agency's publication on the safe-handling of radioisotopes.[72]

VII. COUNTING TECHNIQUES FOR THE RADIOACTIVE SULFUR ISOTOPE

Table I of this monograph shows the nuclear characteristics of each of the known radioactive isotopes of sulfur. Their radioactivities can be measured by either standard Geiger-Mueller, gamma scintillation, or proportional counting techniques.[73-76]

Sulfur-35, 88 d, is most frequently determined in sulfur radiochemistry. Its very weak beta radiations of 0.167-Mev energy have most often been determined by Geiger-Mueller or proportional beta counting.[73,75] More recently, liquid scintillation counting has been used to determine S^{35} in biological tissues, fluids, and extracts.[77] Balmer's studies[48] using S^{35} have also been completed by liquid scintillation counting.

Gamma scintillation spectrometry has been used to complete radio-activation analyses[78,79] of trace stable sulfur. In this work, the 3.1-Mev gamma radiations from S^{37} (5.04 m) were measured directly and quantities of sulfur as small as 10 micrograms have been determined in a variety of sample materials by this method.[80]

VIII. RADIOCHEMICAL PROCEDURES FOR THE SULFUR RADIONUCLIDES

Radiochemistry can generally be described as being an analysis technique used primarily either (1) to assist in obtaining a pure radionuclide in some form so that an absolute measurement of its radioactivity, radiation energies and half-life can be made, or (2) to determine the amount of radioactivity of a particular radioelement in a radionuclide mixture, or (3) to complete a radioactivation analysis being used to determine the concentration of a specific stable element in a particular sample material. In radiochemistry, the desired radionuclide may be isolated and separated by either carrier or carrier-free methods.

Carrier methods are used most frequently in radiochemistry. They involve the addition of a small amount of inactive stable element to a solution of the irradiated material to serve as a carrier of the radionuclide of

that element through the separation method. <u>Carrier-free</u> separations are used most often in those analyses that require that the radioelement be isolated in a manner capable of giving either no amount or a minimal amount of stable element in the final form to be used in the radioactivity measurements.

In most instances, analytical radiochemistry uses separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electroanalysis. However, one major difference exists between carrier radiochemistry and more conventional analytical techniques in that it is not always necessary to recover <u>completely</u> the added amount of <u>carrier</u> element, since a radiochemical analysis is designed to assure that the atoms of a radioactive element achieve an isotopic state with the atoms of the inactive element and any loss of the radioactive species is proportional to the "loss" of carrier during the separation process. Colorimetric, polarographic and similar analysis techniques are seldom used in radiochemistry because they do not separate the desired radionuclide from contaminants (either radioactive or stable) in the mixture being analyzed.

Both <u>carrier</u> and <u>carrier-free</u> methods have been used to measure the radioactivity of sulfur-35 either following its isolation as a tracer[51-58,65,81] or separate it from fission products[82] or from sea water[83] or in radioactivation analyses methods used to determine trace stable sulfur.[78,79] The radioactivation analysis method has been used to determine sulfur in arsenic,[84,85] biological materials,[86] chromium,[84,85] graphite,[85,87] magnesium,[88] organic materials,[89] aluminum phosphate,[85] nitrobenzene,[85] lithium,[85] stainless steel,[85] niobium,[85] terephthalic acid,[85] KOH-HF mixtures,[85] nitrocellulose,[85] ceramics,[85] Zr and Na fluorides,[85] gallium arsenide,[85] indium arsenide,[85] silicon,[85] nickel,[85] copper,[85] HF[85] and asbestos.[85]

The solvent extraction method suggested by Wilk[51] (described in Procedure 1) is a good method for the preparation of carrier-free S^{35} from metallic chloride targets. Wilk[51] also reports on a distillation method and describes the apparatus used for the separation of S^{35} from neutron-irradiated potassium and sodium chloride targets (described in Procedure 2).

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Ion-exchange methods for the preparation of carrier-free S^{35} have also been suggested.[53-58] However, in most instances, large amounts of the S^{35} were found to absorb on the resin. Thus, none of these procedures are included in this Section. The paper chromatography method mentioned elsewhere in this monograph[65] is not included in the list of radiochemical procedures that follow because of similar difficulties.

The carrier methods developed by most researchers involve the precipitation of S^{35} with either barium nitrate or benzidine chloride solutions. These methods are described in some detail in the other Procedures given in this Section. However, it should be noted that the radiochemical procedures employed by Gibbons,[85] Tobias, et al,[86] Lvov and Neumova,[87] Atchison and Beames,[88] and Seaborg and Livingood[89] are similar to those reported in Procedures 4, 5 and 6. For that reason details of these separation procedures are omitted from this Section.

In all instances, pertinent information about the type of targets, length of irradiation, preparation of reagents, radioactivity measurements, etc., is given in order to assist other analysts in their evaluation of each method.

PROCEDURE 1

Procedure Used In: Preparation of radioactive tracers

Method: Solvent Extraction

Element Separated: S^{35} (88 d)

Type Material Bombarded: Ferric Chloride

Type of Nuclear Bombardment: $Cl^{35}(n,p)S^{35}$

Procedure By: Wilk[51]

Separation Time: A few minutes

Chemical Yield of Carrier: Carrier free

Decontamination: Radiochemically purity possible

Equipment Required: Apparatus described by author[51]

Procedure:

1. Dissolve $FeCl_3$ in a few milliliters of conc. HCl. Add 30% H_2O_2 to oxidize all of the iron to Fe^{+3}. Adjust acidity with distilled water to 6 M HCl.

2. Add 1/4 volume of isopropyl ether. Extract S^{35} from the solution by shaking. (Note 1) Repeat isopropyl ether addition and extraction.

3. Strip the ether phase(s) with distilled H_2O. Aliquot water phase for S^{35} radioactivity measurement by G-M counting.

Notes:

1. Ferric Chloride does not extract.

PROCEDURE 2

Procedure Used In: Preparation of radioactive tracers

Method: Distillation by use of hydrogen chloride gas

Element Separated: S^{35}(88 d)

Type Material Bombarded: Sodium or Potassium chloride

Type of Nuclear Bombardment: $Cl^{35}(n,p)S^{35}$

Procedure By: Wilk[51]

Separation Time: A few minutes

Chemical Yield of Carrier: Carrier free

Decontamination: Radiochemically purity possible

Equipment Needed: Extraction apparatus described by author[51]

Procedure:

1. Place the irradiated chloride compound in the salt flask of the extraction apparatus (Note 1).

2. Adjust the over flow through the apparatus, then connect the HCl gas cylinder to the apparatus.

3. Collect the HCl gas (Note 2) in a flask (Note 3).

4. After extraction has been finished, wash the water of the flask with HCl.

5. Evaporate to small volume; aliquot solution for measurement of S^{35} by G-M counting.

Notes:

1. See Wilk's[51] description of apparatus.

2. NaCl and KCl are insoluble.

3. Cooling jacket contains brine cooled by dry ice.

PROCEDURE 3

Procedure Used In: Preparation of Radioactive tracers

Method: Precipitation

Element Separated: S^{35}(88 d)

Type Material Bombarded: Ferric Chloride

Type of Nuclear Bombardment: $Cl^{35}(n,p)S^{35}$

Procedure By: Rudstam, et al.[81]

Separation Time: Short

Chemical Yield of Carrier: Quantitative

Equipment Needed: Standard

Procedure:

1. Dissolve ferric chloride target in a small volume of conc. HCl. Adjust to 1 $\underline{M}$ HCl with distilled water.

2. Add SO_4^{--} carrier solution (10 mgs SO_4^{--}).

3. Add, a few milliliters of $Ba(NO_3)_2$ solution to precipitate $BaSO_4$. Centrifuge; discard the supernatant liquid.

4. Metalhesize by boiling in 10 ml of 50% K_2CO_3 solution. (Note 1). Centrifuge; discard ppt.

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5. Make the supernatant liquid 1 $\underline{M}$ in HCl and then add $Ba(NO_3)_2$ to reprecipitate $BaSO_4$.

6. Wash the $BaSO_4$ several times with water. Collect on a tared filter paper. Weigh for chemical yield.

7. Mount for counting on a G-M counter.

Notes

1. $BaCO_3$ serves as a scavenger for other radioactivities.

PROCEDURE 4

Procedure Used In: Separation of S^{35} from Fission Products

Method: Precipitation

Element Separated: S^{35}(88 d)

Type Material Analyzed: Fission Product Solution

Type Nuclear Bombardment: S^{35} originated from either sulfur or chlorine contamination of uranium fuel. Produced by Neutron reactions: $S^{34}(n,\gamma)S^{35}$ or $Cl^{35}(n,p)S^{35}$

Procedure By: Henriques, et al.[82]

Separation Time: Not estimated by author

Chemical Yield of Carrier: Quantitative

Equipment Needed: Standard

Procedure:

1. Add S^{-2} to aliquot of the fission product solution. Oxidize S^{-2} to SO_4^{-2} by adding a few drops of Br_2 to the solution and heating. Then add a few ml of conc. HCl and evaporate to near dryness.

2. Dissolve the residue in a few milliliters of H_2O; then add Zr^{+3} carrier solution and 1 ml of HF. Precipitate the SO_4^{-2} ions from this mixture by adding dropwise a 2% aq. solution of benzidine chloride (Note 1)

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to precipitate benzidine sulfate. Centrifuge, discard the supernatant liquid.

3. Dissolve the benzidine sulfate precipitate in 1-2 ml of 6 $\underline{M}$ NaOH; add Fe^{+3} carrier to precipitate $Fe(OH)_3$. Centrifuge; discard the precipitate.

4. Transfer the supernatant liquid to an extraction flask, then add an equal volume of isopropyl ether to the flask. Extract the benzidine by shaking. Allow the phases to separate. Discard the organic phase.

5. Neutralize the aqueous phase with a few drops of HCl and add benzidine chloride to reprecipitate the SO_4^{-2} ions as benzidine sulfate. Centrifuge; discard the supernatant liquid.

6. Wash the precipitate with water and ethanol. Collect the precipitate on a tared filter paper. Weigh to determine chemical yield.

7. Mount for counting. Measure the S^{35} radioactivity in a G-M counter.

Notes:

1. Prepared by dissolving 5 grams of benzidine hydrochloride in 40 ml of 1 $\underline{M}$ HCl and diluting with enough 50 per cent alcohol to make 250 milliliters of solution.

PROCEDURE 5

Procedure Used In: Separation of S^{35} from Fission Product Mixture in sea water

Method: Precipitation and distillation

Element Separated: S^{35}(88 d)

Type Material Analyzed: Sea water; Probable origin: $S^{34}(n,\gamma)S^{35}$ or $Cl^{35}(n,p)S^{35}$

Procedure By: Love and Sam[83]

Separation Time: Short

Chemical Yield of Carrier: Quantitative

Equipment Needed: Apparatus described by author[83]

Procedure:

1. To a 10-ml aliquot of sea water add 0.5 ml of conc. ammonium hydroxide and 5 ml of H_2O_2. Boil; then cool and add enough distilled water to make the volume 500 ml.

2. Add slowly 1 ml of conc. HCl and 5 ml of 1 $\underline{M}$ barium chloride solution to precipitate barium sulfate. Filter, collect the barium sulfate precipitate on filter paper circle.

3. Transfer the precipitate and the filter paper to the 200-ml flask of the reduction apparatus (Note 1). Add 50 ml of concentrated hydriodic acid and reflux until all of the barium sulfate dissolves. Absorb the H_2S gas in a second flask filled with 75 ml of 1 $\underline{N}$ NaOH.

Notes:

1. Authors[83] describe apparatus used and its mode of operation for this method.

4. Expel the H_2S from this flask by adding 20 ml of concentrated HCl and collect with suction, the hydrogen sulfide gas in another flask which contains 25 ml of conc. NH_4OH and 60 ml of 30% H_2O_2.

5. Transfer the contents of this flask to a 1-liter flask containing 200 ml of distilled water. Boil to drive off excess ammonia and hydrogen peroxide.

6. Cool, then add 0.5 ml of conc. HCl and 5 ml of 1 $\underline{M}$ barium chloride to precipitate the barium sulfate. Digest. After digestion, filter the mixture through a preweighed No.42 Whatman filter paper circle.

7. Wash the precipitate twice with hot water, ethyl alcohol, and acetone. Dry in an oven at 105°C; cool in a desiccator, and weigh.

8. Mount paper and precipitate for counting on a low background beta counter.

Procedure Used In: Radioactivation analysis

Method of Separation: Precipitation

Element Separated: S^{35}(88 d)

Type of Material Analyzed: Arsenic, chromium, graphite, phosphates and other materials[85]

Type of Nuclear Bombardment: $S^{34}(n,\gamma)S^{35}$

Procedure By: Leddicotte[85]

Chemical Yield of Carrier: At least 65%

Time of Separation: 2 hours

Degree of Purification: Excellent (10^5 or greater) from most radionuclides

Equipment Required: Standard

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 1) and comparator (Note 2) samples in a neutron flux of at least 6.5×10^{11} n/cm²/sec for 1 week or longer (Note 3). Prepare the test and comparator sample for the irradiation either by wrapping each specimen in aluminum foil or placing it in quartz ampoule. Liquid samples should be irradiated in polyethylene bottles (Note 4).

B. Preparation of Irradiated Materials for Analysis

I. The Comparator Sample

1. After the irradiation, quantitatively transfer the comparator sample (Note 2) to a 50-ml volumetric flask. Dissolve the sample in a small, measured volume of 6 $\underline{M}$ HNO_3; then dilute the solution to 50 ml with water. Mix the solution well by carefully shaking it.

2. By means of a volumetric pipet, pipet a 1.00-ml aliquot of it into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same centrifuge tube, 2.00 ml of a standard carrier solution of known sulfur concentration (Note 5). Also, add 1 ml each of holdback carriers of barium, cadmium, cobalt, copper, iron, manganese, phosphorus, sodium, and zinc (Note 6). Dilute the solution to 20 ml with water, mix it well and make the solution 0.3 $\underline{M}$ in HCl. Continue with Part C below.

II. Solid Test Sample

1. If the sample is a metal or alloy, quantitatively transfer the irradiated test portion from the quartz tube or aluminum wrap to a 50-ml glass centrifuge tube, and then add, by means of a volumetric pipet, to the same centrifuge tube 2.00 ml of a standard carrier solution of known sulfur concentration (Note 5). Also add 1 ml each of holdback carriers of barium, cadmium, cobalt, copper, iron, manganese, phosphorus, sodium and zinc (Note 6). To this mixture, add dropwise enough concentrated mineral acid to completely dissolve the sample (Note 7). Dilute the solution to 20 ml with water, mix it well and make the solution 0.3 $\underline{M}$ in HCl. Continue with Part C below.

III. Liquid Test Samples

1. Pipet an aliquot of the irradiated portion into a 50-ml glass centrifuge tube. By means of a volumetric pipet, add to the same centrifuge tube 2.00 ml of a standard carrier solution of known sulfric concentration (Note 5).

C. Radiochemical Separation of S^{35}

1. Oxidize S^{-2} to SO_4^{-2} by adding a few drops of Br_2 to the solution and heating. Then add a few ml of conc. HCl and evaporate to near dryness.

2. Dissolve the residue in a few milliliters of H_2O; then add Zr^{+3} carrier solution and 1 ml of HF. Precipitate the SO_4^{-2} ions from this mixture by adding dropwise a 2% aq. solution of benzidine chloride (Note 8) to precipitate benzidine sulfate. Centrifuge, discard the supernatant liquid.

3. Dissolve the benzidine sulfate precipitate in 1-2 ml of 6 $\underline{M}$ NaOH; add Fe^{+3} carrier to precipitate $Fe(OH)_3$. Centrifuge; discard the precipitate.

4. Transfer the supernatant liquid to an extraction flask, then add an equal volume of isopropyl ether to the flask. Extract the benzidine by shaking. Allow the phases to separate. Discard the organic phase.

5. Neutralize the aqueous phase with a few drops of HCl and add benzi-

dine chloride to reprecipitate the SO_4^{-2} ions as benzidine sulfate. Centrifuge; discard the supernatant liquid.

6. Wash the precipitate with water and ethanol. Collect the precipitate on a tared filter paper. Weigh to determine chemical yield.

7. Mount for radioactivity measurements.

D. **Measurement of S^{35} Radioactivity and Calculation of Stable Sulfur Content of Test Sample**

1. The S^{35} radioactivity in both the test and the comparator samples is assayed by beta counting. Use a Geiger-Mueller counter for the beta measurements.

2. Following the radioactivity measurements, correct the observed S^{35} radioactivity for decay, dilution volume(s), and the sample weights (or volumes) of both the test and comparator samples. A simple ratio of these corrected radioactivities becomes a measurement of the amount of stable sulfur in the test sample:

$$\% \text{ S in Test Sample} = \frac{\text{Corrected } S^{35} \text{ radioactivity in Test Sample}}{\text{Corrected } S35 \text{ radioactivity in Comparator Sample}} \times 100.$$

Notes:

1. Solid test samples should weigh from 0.10 - 0.20 gram; liquid samples should have a volume of from 5 - 25 milliliters.

2. Use 0.025 to 0.030 grams of spectrographically pure ammonium sulfate.

3. The limits of measurement for stable sulfur by this procedure is 1×10^{-5} gram.

4. Irradiations of liquid, vegetation, or similar type sample materials must be made in an air-cooled or water-cooled reactor irradiation facility.

5. Standardized to contain at least 10 milligrams of sulfur per milliliter.

6. Solutions of the ions of other elements may also be added as holdback carriers; concentration equal to 5 milligrams of element per milliliter.

7. Soils, clays, and similar materials may require addition of HNO_3 or fusion.

8. Prepared by dissolving 5 grams of benzidine hydrochloride in 40 ml of 1 $\underline{M}$ HCl and diluting with enough 50 per cent alcohol to make 250 milliliters of solution.

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