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ABSTRACT

Most high-level liquid wastes at the Savannah River Plant (SRP) are byproducts from plutonium and enriched uranium recovery processes. The high-level liquid wastes generated by these separations processes are stored in large, underground, carbon-steel tanks. The liquid wastes consist of: supernate (an aqueous solution containing sodium, nitrate, nitrite, hydroxyl, and aluminate ions), sludge (a gelatinous material containing insoluble components of the waste, such as ferric and aluminum hydroxides, and mercuric and manganese oxides), and salt cake (crystals, such as sodium nitrate, formed by evaporation of water from supernate). Analyses of SRP wastes by laser-Raman spectrometry, atomic absorption spectrometry, spark-source mass spectrometry, neutron activation analysis, colorimetry, ion chromatography, and various other wet-chemical and radiochemical methods are discussed. These analyses are useful in studies of waste tank corrosion and of forms for long-term waste storage.

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INTRODUCTION

The high-level, radioactive aqueous wastes from onsite reprocessing of fuel irradiated in Savannah River Plant (SRP) reactors are stored initially as liquids or slurries in buried, double-wall, carbon-steel tanks. Each tank has a capacity of 750,000 to 1,300,000 gal. This report discusses the analyses of the wastes necessary to support various corrosion studies and the candidate solid forms for long-term storage of the wastes.

The general approach to this problem has been to develop methods that will give the analytical quality needed, not necessarily the best answer available. With this approach, turnaround is more rapid, charge- and mass-balance are reasonable, and costs and radiation exposures to personnel are minimized.

Origins of SRP Radioactive Liquid Waste

Most of the liquid radioactive waste at SRP originates in the two separations plants (Figure 1), although some liquid waste is produced in the reactor areas, laboratories, and peripheral installations. The principal processes used in the separations plants have been the Purex and the ^{235}U processes described by Karraker[1] and Siddall,[2] but other processes have been used for a variety of fuel and target elements. The Purex process recovers and purifies uranium and plutonium from neutron-irradiated natural uranium. The ^{235}U process recovers enriched uranium from uranium-aluminum alloys used as fuel in SRP reactors.

Other processes that have been used include: recovery of ^{233}U and thorium (from neutron-irradiated thorium), recovery of ^{237}Np and ^{238}Pu, separation of heavier actinide elements from irradiated plutonium, and recovery of enriched uranium from stainless-steel-clad fuel elements. Each of these processes produces a characteristic liquid waste. Furthermore, each process produces both high-activity waste (HAW) and low-activity waste (LAW), that have been segregated for storage. High activity refers to waste that originates in process steps that remove most of the fission products as waste; low-activity wastes are produced in other process steps and have fission-product contents less than

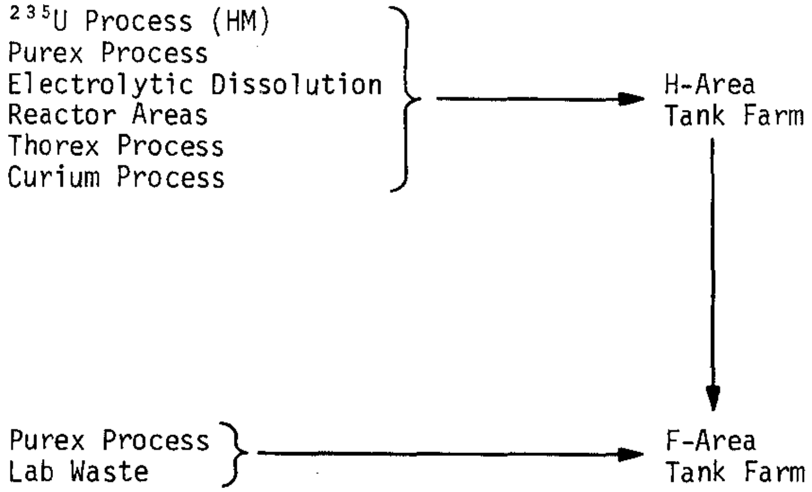

FIGURE 1. Origins of SRP High Level Liquid Waste

0.1% that of high-activity waste. The distinction between high- and low-activity waste at SRP has almost vanished because of mixing from transferring waste from one tank to another.

Most wastes from these processes are acidic; however, before transfer to the mild steel storage tanks, they are neutralized with sodium hydroxide. After the waste is neutralized and transferred to cooled tanks, insoluble oxides and hydroxides of fission products and of metals (e.g., iron, mercury, and manganese from chemical processing) settle to form a sludge layer. The volume of the sludge is about 10% of the total waste volume; the remainder (supernate) principally consists of solutions of sodium salts used in processing or formed when the acid wastes are neutralized.

In recent years, water has been evaporated from aged supernates and the remaining salts returned to cooled tanks where a portion crystallizes. This procedure reduces waste volume and renders the waste less mobile.

General Chemical Composition of Waste

Although each recovery process produces a characteristic waste (Appendix A), development of a meaningful generalization of waste composition based on flowsheet or process analysis is impossible because of mixing (to conserve storage volume), radiation-induced changes in composition, evaporation, precipitation of insoluble constituents (sludge), and subsequent removal of sludge from some tanks.

An estimate of the concentrations of major chemical components in the waste tanks (Table 1) is calculated on the basis that all of the salt is dissolved, and the remaining solution is mixed uniformly with the sludge. Aluminum exists in both sludge and supernate, and the amount in each depends on the aluminum and sodium hydroxide concentrations in each tank. This estimate guided the development of the analytical procedures discussed in this report.

TABLE 1

Chemical Composition of Waste

Constituent	*Concentration, M*	*Constituent*	*Concentration, M*
$NaNO_3$	2.2	MnO_2[a]	0.02
$NaNO_2$	1.1	NaF	0.02
$NaAlO_2$	0.8	Na_3PO_4	0.01
NaOH	0.5	NaCl	0.01
Na_2CO_3	0.3	KNO_3	0.01
Na_2SO_4	0.3	$CaCO_3$[a]	0.006
$Fe(OH)_3$[a]	0.15	HgO[a]	0.002
		$Mg(OH)_2$	0.001
		NaI	0.0002

---

[a] Predominantly in the sludge; other constituents are predominantly in the supernate.

Obtaining and Handling Waste Samples

Supernate samples were obtained by pumping waste supernate from a tank into a sampling loop and back into the tank. The intake from the pump was about 0.5 m below the liquid surface. Samples were taken after supernate had been pumped through the loop for several minutes.

Sludge surface samples were obtained using a modified, river-bottom, sludge-sampling, clam-shell device. Subsurface sludge samples were obtained using a sealed sampler which was opened at the desired depth in the sludge to take a sample and then resealed before return to the surface. Details of the sludge sampler design and the subsurface sampling procedure are given elsewhere.[3]

An attempt was made to handle the samples in a manner corresponding as closely as possible to the proposed handling in a conceptual waste processing plant (Figure 2). As interstitial solution was obtained with the sludge samples, the solution was separated by centrifugation and reserved for analysis and comparison to supernate. One conceptual design process calls for drying of the centrifuged raw sludge followed by two wash-dry cycles. Therefore, samples of dry, centrifuged, raw sludge; the two water wash solutions; and the twice-washed, dried sludge were analyzed individually. Sample handling was consistent with this conceptual design.

This procedure was also scaled up from the gram-range to the kg-range. Details of the kg-range sludge washing and drying are given elsewhere.[3]

ANALYTICAL METHODS AND RESULTS

Detailed chemical and radiochemical analyses have been completed for surface sludge samples from Tanks 7 and 16; subsurface sludge samples from Tanks 5, 7, 13, 15, and 16; and supernates from Tanks 1, 2, 4, 5, 6, 8-15, 18, 21, and 24. Details concerning the waste compositions in many of these tanks are given elsewhere;[3-5] summaries are given in Appendix A. Detailed analytical procedures are given in Appendix B. While this report was in press, some procedures were changed. The revised methods are given in Appendix C.

Stable-Element Species

Supernates and Interstitial Solutions

Polyatomic Anion Determinations

Raman Spectrometry

Polyatomic anions in the supernate and interstitial solutions were determined by a laser-Raman spectrometric method developed by A. L. Marston. The liquid samples were clarified by centrifugation, contained in conventional 1-mm-ID glass capillaries, and sealed with *Apiezon** wax.

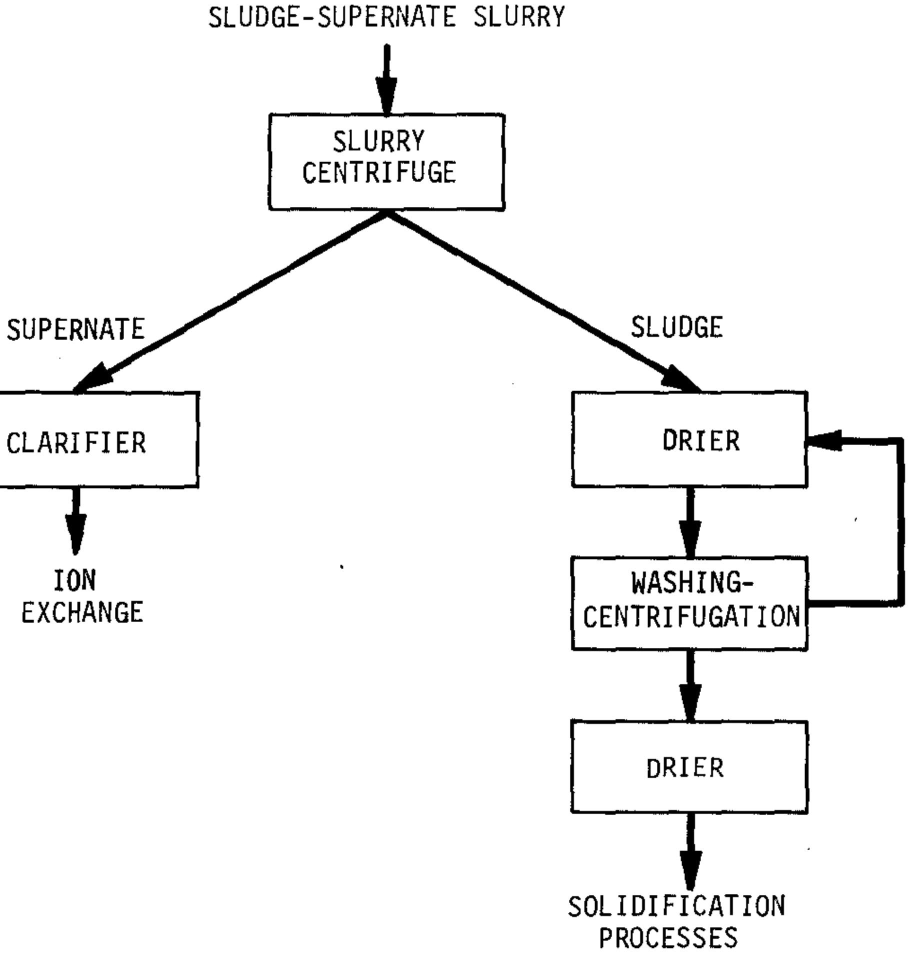

FIGURE 2. Sludge-Supernate Separation

The high concentration of nitrate ion in high-level radioactive waste supernate is used as an internal standard to determine relative concentrations in nitrite, sulfate, chromate, phosphate, and aluminate ions. An independent determination of the nitrate ion in the radioactive waste sample then is made by mixing appropriate aliquots with standard 2M $NaClO_4$ and measuring the 1050 Δcm^{-1} nitrate ion peak relative to the 935 Δcm^{-1} perchlorate ion peak at known concentration. Relative anionic concentrations are converted to absolute concentrations based on the independent nitrate ion analysis.

Figure 3 shows the Raman spectrum of a synthetic sample in juxtaposition with that of a typical high-activity waste supernate. Although the sample matrix was complex, spectral interferences were small and could be avoided by proper choice of analytical peaks. The more-intense nitrite ion peak at 1332 Δcm^{-1} cannot be used because it is overlapped by the 1358 Δcm^{-1} nitrate ion peak. The nitrite ion peak at 818 Δcm^{-1} was free of interferences and gave reproducible results. At concentrations above 0.5M, the sulfate ion peak at 613 Δcm^{-1} will interfere with the aluminate ion peak at 622 Δcm^{-1}, but the sulfate ion concentrations rarely exceeded 0.1M.

Strongly alkaline waste solutions absorb carbon dioxide from air sparges to form carbonate ions. Unfortunately, the major carbonate ion peak at 1070 Δcm^{-1} is strongly overlapped by the more-intense nitrate ion peak at 1050 Δcm^{-1}.

Free hydroxyl ion produces a sharp Raman peak that appears as a shoulder at 3615 Δcm^{-1} on the high frequency side of the H_2O stretching bands. This peak could be resolved with a curve resolving instrument; but because of other methods developed, this was not necessary.

Typical analyses are given in Table 2. Note that the only really significant change between supernate and interstitial solution is the increase of the nitrite-to-nitrate ratio. This higher ratio is to be expected because most of the activity resides in the sludge, and nitrite is the radiolytic degradation product of nitrate.

Extensive cross-checking with other methods indicated the accuracy for detecting aluminate, nitrate, nitrite, sulfate, chromate, and phosphate ions was about ±10% for sample volumes of only 1 to 2 μL. The relative precision at the 95% confidence level for a single determination was ±5%.

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*Tradename of James G. Biddle Co., Plymouth Meeting, Pa.

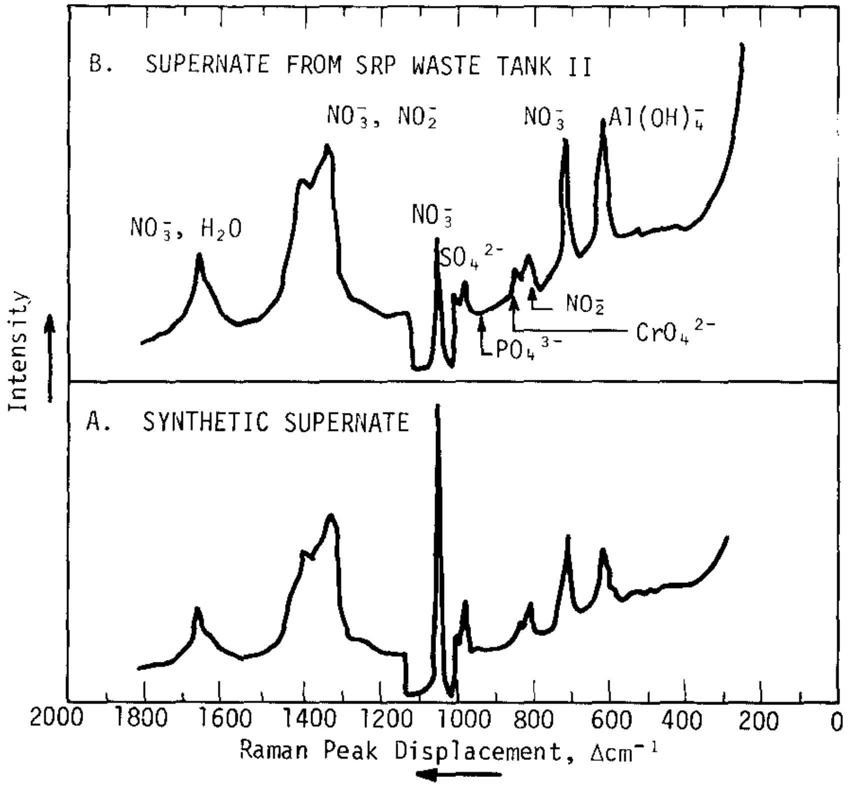

FIGURE 3. Raman Spectra of Waste Supernates

In general, the useful detection range for nitrate and nitrite ions in concentrations is $\geq 0.01M$; for aluminate and phosphate ions, $\geq 0.02M$; and for chromate and sulfate ions, $\geq 0.001M$. Raman analysis, was our standard method for analyzing these six ions in basic solutions. The new ion chromatographic method is described in Appendix C.

pOH Determinations

When measuring pOH concentrations in concentrated salt solutions, an inherent error will exist with normal calibration procedures. These calibration procedures require buffers of low ionic strength and assume that a constant liquid-junction potential exists for both calibration and measuring solutions. However, in these waste solutions the presence of dissolved salts will result in a change in the junction potential and, hence, an error in the measured pH. Furthermore, the glass electrode is affected by the sodium ions present in these alkaline solutions.

TABLE 2

Typical Raman Analyses

	Concentration, M			
Anion	*Supernate*	*Interstitial Solution*	*First Wash*	*Second Wash*
NO_3^-	3.7	2.27	0.16	0.16
$Al(OH)_4$	0.9	0.6	0.09	0.009
NO_2^-	0.6	1.3	0.09	ND[a]
CrO_4^{2-}	0.005	0.004	ND	ND
PO_4^{3-}	0.02	ND	ND	ND
SO_4^{2-}	0.08	0.05	0.0034	0.0003
CO_3^{2-}	0.1	0.2	ND	ND

---

[a] ND, not detected.

Hydroxide concentrations were determined by E. W. Baumann's method of pH determination in concentrated salt solutions[7] and by titration of free base (above pH 13) as discussed in the next section. The procedure required salted buffers whose empirical pH values (in terms of concentration) were determined by calibration with known concentrations of HCl or NaOH in the salt solutions. The stock (Beckman pH 10) buffer solution was found to have a measured pH of 9.75 in a 4M sodium nitrate solution. With the conventional method of calibration with a low ionic strength standard buffer, the results were similarly low. The results also varied with the type of liquid junction at the reference electrode.

When the potentials are measured as a function of added hydrogen and hydroxyl ions, the ion concentration product of water in these salted solutions can be estimated. Thus, pOH values can be derived from pH measurements. For concentrated salt solutions, this value differs from the generally used value of $10^{-14.00}$, the thermodynamic dissociation of water at 25°C. In 4M sodium nitrate solutions, the calculated value of the ion product was $10^{-14.10}$.

Aluminate, Carbonate, and Hydroxyl Ions by Titration

The above pH method gave excellent results for hydroxyl ion concentrations over the pH range of 10 to 13. However, in the highly salted solutions above pH 13, the error of ±0.1 pH unit becomes significant in calculating the total free hydroxide concentration. A titration method was developed to permit the determination of hydroxide under these conditions, and at the same time permit determination of aluminate and carbonate ion concentrations (see pg. 112).

To titrate the free base at these higher concentrations, the carbonate ions were first precipitated by adding barium chloride. After centrifugation and decanting the mother liquor, the carbonate ion concentration was determined by dissolving the residue in a known aliquot of standard acid and then back titrating with standard base. Both the free hydroxyl ion and the aluminate ion concentrations were then determined by first adjusting the hydroxide and aluminate solutions to pH 7; complexing the aluminum with oxalate ion,[8] and then titrating the solution to pH 7.

Results of duplicate analyses of a series of high-level waste solutions, determined on 50 μL samples, are given in Table 3. The relative standard deviations of 2 to 5% for this series are indicative of the ranges of precision to be expected for analyses of high-level waste samples by these procedures.

The effect of interferences on these procedures was also investigated. Sulfate does not interfere with the analysis. Barium sulfate precipitates along with the carbonate and does not dissolve in the excess acid needed. Phosphate interferes when the carbonate is determined by the procedure described, which designates the titration end point as pH 7. Barium phosphate preciptates with the barium carbonate but subsequently dissolves in the added acid. Because the phosphate does not decompose on heating, the resulting phosphoric acid makes part of the excess acid inaccessible to titration and also shifts the end point. Differential methods can be used to make a phosphate correction.

Sulfate Ion Determinations

Sulfate was the only ion determined by a turbidity method. The dissolved sludge samples required the removal of the interfering ions and elements before a reasonable analysis could be made. The high apparent sulfate analyses obtained by this method for the dissolved sludge samples was caused by the complex $FeCl_4^-$. The yellow-colored complex had an absorbance at 380 nm, the wavelength used for the turbidity method.

TABLE 3

Precisions of Aluminate, Carbonate, and Hydroxyl Analyses

Sample	*Concentration of Constituent, M*					
	$Al(OH)_4^-$		CO_3^{2-}		OH^-	
1	0.295	0.305	0.200	0.200	1.254	1.184
2	0.356	0.350	0.152	0.171	0.412	0.422
3	0.550	0.560	0.137	0.142	7.595	7.580
4	0.466	0.514	0.088	0.090	6.884	6.720
5	0.198	0.181	0.127	0.128	2.505	2.587
6	0.101	0.105	0.081	0.085	1.680	1.631
7	0.112	0.103	0.104	-	1.656	1.648
RSD[a], %	5.0		5.1		1.7	

---

[a] Relative standard deviation.

For supernate and interstitial solutions, sodium nitrate was the only major interference to a barium sulfate turbidity method for the analysis of sulfate ion. Because dilution of the sample with water appeared to make the sodium nitrate interference negligible, sulfate ion concentrations in supernate and interstitial solutions were cross-checked on a random basis by a barium sulfate turbidity method.[9] The limit of detection is about 0.002M SO_4^{2-} with a precision of about ±10%.

In general, a sample aliquot is added to a mixture of barium chloride, sodium chloride, ethanol, and glycerol, and the absorbance was determined at 380 nm. These readings are compared to a standard curve prepared by the same analytical method.

Colorimetric Methods

Colorimetry was used to cross-check the laser-Raman nitrate ion[10] and nitrite ion[11] analyses and provided the only method of analysis when solutions fluoresced in the laser beam.

In general, nitrite analyses are performed by coupling the diazonium ions (formed by diazotation of sulfanilamide by nitrite in a buffered acidic solution) with N-(1-naphthyl)-ethylenediamine to produce a reddish-purple color. The color intensity is measured with a spectrophotometer at 540 nm. The method is applicable to solutions containing ≥0.25 mg NO_2^-/L. The only known interferences are strong oxidants (e.g., potassium permanganate) or reductants (e.g., ferrous ion). High alkalinity (>600 mg OH^-/L) will also give low results due to a shift of the color reaction caused by pH changes. Partial neutralization of the sample aliquot will prevent this shift.

The precision and accuracy were not determined. Cross-check analysis with Raman and duplicate analysis by colorimetry, however, generally agreed within ±5%.

Nitrate analyses were preformed by the commonly known "brown ring" reaction. The nitrate ions in the sample were reacted with ferrous ammonium sulfate and sulfamic acid in the presence of 15M sulfuric acid to form ferrous nitrosyl sulfate ($FeSO_4 \cdot NO$). The absorbance of the resulting red solution is read on a spectrophotometer at 530 nm.

The method is applicable to solutions containing ≥ 0.3 mg NO_3^-/mL. The precision and accuracy of the method is generally about ±3 to ±5%.

Monoatomic Anion Determinations

Chloride and fluoride ions are the only two stable monoatomic anions which exist in SRP waste solutions at concentrations that can be determined by normal wet chemical methods. Both of these anions were determined by specific-ion electrode methods.[12]

In general, metal ions which mask either fluoride or chloride ions are complexed with phosphate ion, and the anion concentrations are determined by the method of standard additions. In SRP waste, the method is applicable to samples containing ≥ 50 ppm F^- or Cl^- with a precision and accuracy of about ±10%.

Analyses of Supernate and Interstitial Solutions for Cations

The major cation in both the supernate and interstitial solutions is sodium; minor cations are potassium and calcium. These three elements are determined by normal atomic absorption methods. Because a thousandfold dilution is normally necessary to dilute the ^{137}Cs to acceptable levels for the atomic absorption laboratory, the limit of detection for these elements is ~ 1000 ppm. The precision and accuracy are about ±5%.

Trace cations (<1%) included Th, U, Ag, Pb, Fe, and ammonium. Colorimetric methods (see Appendix B) were used to determine Fe,[13] Th,[14] U,[15] and ammonium.[16] The precision and accuracy of these methods was generally about ±5%. Uranium was also determined by fluorescence.[17] Isotope-dilution and spark-source mass spectrometry were used to determine silver.[5] The precision of this method was about 40%. A cathodic stripping analysis technique, with a precision and accuracy of about ±5%, was used to determine lead concentrations.[18]

Sludge

Preparation of Samples for Analysis

Drying Sludge

Raw sludge contains ~80 wt % soluble sodium salts such as the hydroxide, nitrate, nitrite, aluminate, and sulfate. The remaining 20 wt % is made up of the hydrous oxides, hydroxides, and oxyanions of Fe, Al, Mn, Ca, U, Hg, and Ni. A drying temperature of 1200°C is necessary to remove water of crystallization and hydroxyl water from this mixture of compounds.[19] However, to dry the sludge totally would result in the decomposition and/or distillation of sodium hydroxide, sodium nitrate, sodium nitrite, mercury, and perhaps other elements of major interest. Therefore, for purposes of this study, the dry weight has been defined as the residual weight after drying for 16 hr at 110°C. The dry weight of duplicate samples usually agreed within 5%.

Dissolution of Sludge

Water Soluble Salts. The analyses of the water soluble portion of sludge is desirable for two reasons: (1) it gives an indication of what portion of the sludge can be dissolved and handled in the same manner as supernate, and (2) all methods for total sludge dissolution destroy one or more anions and prevent their analysis.

A reasonable estimate of the nitrate and nitrite concentrations can be determined by first leaching the sample with distilled water followed by either Raman or colorimetric determinations. Even though the method for analyzing leach solutions has a precision and accuracy of ≤10%, the overall precision and accuracy are dependent upon the degree of recovery of the soluble salts by the leaching process. Total recovery of soluble salts was complicated by excessive peptization of the sludge if the pH of the leach solution was reduced below about 10 to 11. This interference is on an analytical level and should not be construed as being excessive peptization on a processing level.

To minimize the peptization problem, 2 to 3 g portions of sludge were leached with four 10-mL washes of distilled water. Each leach batch was agitated on a vortex mixer for 30 to 45 minutes before centrifugation.

As shown in Tables 4 and 5, however, the actual recovery of soluble salts from raw, dried sludge varied from ~60 to 100%; the average recovery was 83% ($\sigma = \pm 12\%$). As a result, the estimate of the nitrate and nitrite concentrations were generally low.

TABLE 4

Recovery of Sodium Ion by Four Leaches

Sample	*Sodium Ion Concentrations*[a] *Total Na^-, g*	*Leachable Na^-, g*	*Recovered by Procedure, g*	*Recovery, %*
5-1	373.4	341.0	309.8	90.8
5-2	430.8	393.4	299.3	76.1
15-1	282.4	279.9	196.8	70.3
15-2	149.5	148.2	142.2	96.0

---

[a] Precision of analyses, ±5%.

TABLE 5

Recovery of Nitrate Ion by Four Leaches

Sample	*Nitrate Ion Concentrations*[a] *Total NO_3^-, g*	*Leached NO_3^-, g*	*Recovery, g*
5-1	483.3	361.6	74.8
5-2	340.1	371.3	109.7
5-3	281.1	211.5	75.2
13-2	443.8	345.4	77.8
13-3	629.5	403.1	64.0
13-4	540.3	430.7	79.7
15-1	355.4	313.7	88.3
15-2	230.9	244.6	105.9

---

[a] Precision of analyses, ±10%.

Total Dissolution of Sludge. For the analysis of metal ions, the sludge was dissolved by three methods: boiling 6M HCl, boiling 15M HNO_3-0.1M HF, and repeated fuming with sulfuric acid. Dissolution of the centrifuged wet sludge was much easier than the dissolution of sludge dried by heating. Also, if the sludge was washed before drying, it was more difficult to dissolve. The overall dissolution behavior indicates that the major difficulty arises from a coating of manganese dioxide on the sludge particles. When this coating is dissolved, the sludge dissolves.

Anion Determinations

Whereas charge balance is relatively easy with the supernates and interstitial solutions, charge and mass balance is complicated by the presence of oxides, oxyanions, hydroxides, hydrates, telomers, polymers, and nonstoichiometric compounds in both the wet and the defined dry sludge.

Charge balance was obtained by estimating the anions by the following methods:

1. Soluble nitrate, nitrite, hydroxide, and chloride compounds are leached from the sludge, and their concentrations are then determined by analyzing the leach solutions. To get good analyses, the sludges are leached 6 to 8 times each.

2. The elements Al, U, Mo, and Cr are determined on the totally dissolved sample and assumed to be present as their oxyanions.

3. Sulfate is determined on the totally dissolved sample after removing it from interferences by column chromatography or by precipitation of interferences with NaOH.

4. Manganese is assumed to be the only true oxide present.

5. Charge balance is then forced by assuming all unaccounted for charge present as hydroxyl ion.

A further refinement in the published Raman procedure[6] was necessary to determine the lower salt concentrations of the leach solutions. Because Raman scattering from water interferes significantly at lower aluminate ion and total salt concentrations by causing baseline uncertainties, the baseline was fixed by using the 720 Δcm^{-1}/1050 Δcm^{-1} peak ratio to reduce the error to <10%. The variability of the bias without this correction is shown in Table 6.

Raman Spectrometry

Raman spectra of the combined leach solutions were routinely obtained. This provided analyses for nitrate and nitrite ions in most cases, and for sulfate, chromate, and phosphate ions in some cases. However, when determinations were made on washed sludge, the last three ions were frequently below the detectable limits of Raman spectrometry (Table 2). An additional change from the normal supernate procedure was to use a dilution factor of 10 instead of 100.

TABLE 6

Comparison of Aluminum Analyses by Different Methods

Aluminum Concentration, Relative			
	Titration		
STD	*H+*	*EDTA*[a]	*Raman*
0.999	0.980	0.944	1.0
0.500	0.459	-	-
0.200	0.198	-	-
-	0.17	0.20	0.36[b] (0.20)[c]
-	0.31	0.38	0.57[b] (0.37)[c]
-	0.19	-	0.26[b] (0.20)[c]

---

a. See Reference 19.

b. Without baseline correction.

c. With baseline correction.

Colorimetric Methods

Colorimetric methods were used to determine nitrate ion[10] and nitrite ion[11] concentrations both in the combined leach solutions and in the HCl dissolution solutions. In all cases, as shown in Table 7, some of the nitrate ions were reduced to nitrite ions during dissolution by HCl. The leach procedure therefore gives much more accurate estimates of the nitrate and nitrite ion concentrations. Colorimetry did provide a cross-check for Raman analyses and provides the only method of analysis when the solutions fluoresce in the laser beam.[17]

TABLE 7

Comparison of Nitrate and Nitrite Ion Analyses by Method of Sample Preparation

	HCl Dissolution		*Leach Solution*	
Sample, 1 kg each	NO_3^-, g	NO_2^-, g	NO_3^-, g	NO_2^-, g
Raw 5-1	61.4	53.8	361.6	1.3
Product 5-1	111.9	0.3	292.9	0.7
Raw 5-2	13.5	1.0	371.3	1.6
Product 5-2	11.5	0.4	155.7	0.8
Raw 5-3	13.6	0.7	211.5	7.1
Product 5-3	6.3	0.3	37.4	2.6

Turbidity Methods

Sulfate was determined using the barium sulfate turbidity method[9] for both the leach solutions and the total dissolution solutions. In all cases determined, not all of the sulfate was in the form of water-soluble salts. Sulfate ion concentrations were determined directly for both the leach and supernate solutions.

For the total dissolved sludge, it was necessary to remove the sulfate ion before analyses to remove the interferences. For the initial work, the Fe, Mn, Ni, alkaline earths, lanthanides, and actinides were precipitated by the addition of a sample aliquot to twice the aliquot volume of 6M NaOH, and the sulfate ion concentration was then determined by the turbidity method. Even though this removal step reduced interferences, it did not eliminate them. However, this method allowed the estimation of sulfate ion concentrations to within a factor of about 2 to 10 (Table 8). Sulfate contents published for Tanks 5, 7, 13, 15, and 16 were determined by this method. Due to the variability of the bias from using this method of separating sulfate ions from the interferences, the cleanup procedure was changed to an alumina column method.[20] In general, the sample aliquot was diluted to about 1M HCl with distilled water and loaded onto an alumina column. The interfering cations passed through the column while sulfate ions were retained. After washing the column, sulfate ions were removed with an ammonia solution and then evaporated to near dryness. The residue was dissolved and analyzed by the turbidity method.[9]

TABLE 8

Comparison of Methods for Analyzing Sulfate Ions

	Sulfate Ion Concentration, wt %	
Sample No.	*NaOH Separation*	*Al_2O_3 Separation*
1270	0.470	0.050
1271	17.32[a]	0.118
1767	0.430	0.046
2052	0.240	0.085
2783	0.140[b]	0.206
3549	0.420	0.238

---

a. Original dissolution was diluted to volume with 6M HCl instead of water; hence, insufficient NaOH was present to precipitate completely the interfering cations.

b. NaOH was added to the HCl solution, instead of the HCl solution being added to NaOH.

Ion-Selective Electrode Methods

Both chloride and fluoride ion concentrations were determined in the leach solutions by ion-selective electrodes using the method of standard additions.[7] In general, metal ions that mask chlorine or fluorine ions were first complexed with phosphate ion. The halogen ion concentration was then determined by comparing the potentials imposed across the electrode when aliquots of a standard solution were added with the potentials imposed when known amounts of the halogen were present in similar salted solutions.

No attempt was made to determine either chloride or fluoride ion concentrations in the totally dissolved sludge samples. The chloride content of the totally dissolved samples was altered by each of the three methods of dissolution. The ratio of masking agents (mainly aluminum and iron) to fluoride was so large that the method gave very erratic results.

pH Methods

As the pH of the leach solutions was less than that of the supernate solutions, the pH determinations in the leach solutions were more accurate than those obtained in the concentrated salt solutions discussed above. The pH determination allows a lower limit for the total hydroxyl ion concentration to be calculated.

Spark-Source Mass Spectrometry (SSMS)

To assure that all anions were determined, all leach and total dissolution solutions were analyzed by SSMS. Concentrations of anions, such as phosphate, molybdate, and tungstate, were then calculated from the SSMS results. Even though the results by this method were accurate only to about a factor of three, the concentrations of these elements were very low; in general, less than 1%.

Cation Determinations

The raw as well as washed sludge was a complex mixture of more than 30 elements. The raw sludge was about 80 wt % soluble sodium salts. The major metallic ions in washed and dried sludge were Fe, Mn, Al, U, Na, Ca, Hg, and Ni (Table 9). One or more of

TABLE 9

Precision of Sodium Ion Analyses

Sample[a]	*Sodium in Total Sample, g*	
	Raw Sludge	*Duplicate*[b]
5-1	373.4	372.1
5-2	430.8	426.6
5-3	360.0	358.8
7-1	321.6	315.6
13-1	377.1	371.5
13-2	375.7	358.3
13-3	384.9	377.7
13-4	343.5	343.7
15-1	282.4	280.4
15-2	149.5	148.3
RSD,[c] %	1.40	
95% Confidence Level, %	2.93	

---

[a] Tank number followed by sample number from that tank.

[b] "Duplicate" is the sum of sodium removed by washing plus sodium remaining in the washed, dried sludge.

[c] Relative standard deviation.

the following techniques were used to determine the major (>10 wt %) and minor (1 to 10 wt %) elements:

1. Spark-source mass spectrometry
2. Atomic absorption
3. Colorimetry
4. Titration
5. Neutron activation analyses

The trace (0.1 to 1 wt %) elements were determined by spark-source mass spectrometry. Many of the trace elements were then determined by atomic absorption. The concentration of micro-trace ($\leq$0.1 wt %) elements was calculated from the SSMS results only.

Spark-Source Mass Spectrometry (SSMS)

SSMS was used as a general elemental survey tool for all samples. Due to the high sodium ion content of raw sludge, SSMS of undissolved raw sludge gave variable low results for total sodium (from a factor of 2 to 10 low from spalling of the sample). However, by taking some of the minor element-to-element ratios that were determined by other techniques, reasonable estimates were calculated for all elements above the SSMS detection limit. Because the sludge was dissolved in HCl, SSMS was the only way to obtain a reasonable estimate for chloride ion. Dissolved raw sludge and both dissolved and undissolved portions of washed and dried sludge were also analyzed by SSMS. In general, all elements that were determined to have trace or higher concentration levels were then analyzed by other techniques. Ultra-trace level elemental concentrations were calculated on the basis of the spark source results.

Atomic Absorption Methods

The major metallic ions (Al, Fe, Na, K, Ca, and Mn) can be determined by the atomic absorption (AA) method in both raw and washed sludge. Due to the ^{137}Cs gamma ray emission, and the fact the instrument is uncontained, most of the minor elements cannot be determined by AA in raw sludge because of the extreme sample dilutions necessary to meet the low radioactivity requirements of AA samples. About 90 to 95% of the ^{137}Cs gamma activity can, however, be removed along with the soluble salts during leaching. After ^{137}Cs removal, dilution factors of 50 to 100 reduce the gamma activity to within the AA laboratory limits.

As the concentration of the minor element is a factor of 2 to 3 greater in the washed sludge than in the raw sludge, many of the trace elements (e.g., Ni, Ba, Ca, K, Hg, Mg, and Cr) can be determined for the contents of many of the tanks. Micro-trace elements cannot be done by AA unless some concentrating chemistry is first performed. To date, there has been no need for better analyses for the micro-trace elements than SSMS can provide and, hence, none have been attempted.

The Na, K, and Ca concentrations were also determined in the leach solutions by AA analyses.

Results of duplicate sodium analyses of a series of waste tank sludges are given in Table 9. The initial column gives the analyses determined on total dissolution solutions of raw, dried sludge. The duplicate analyses column is the sum of the sodium washed out of the sludge plus the analyses determined in total dissolution solutions of washed and dried sludge. The relative standard deviation of 1.40% for this series indicates the precision to be expected for other analyses of high-level waste samples.

Colorimetric Methods

Colorimetric analyses for iron,[13] thorium,[14] and uranium,[15] were routinely performed. For thorium and uranium, colorimetry was the only method used; for iron, colorimetry was used as a cross-check and as a backup method for AA.

Titration Methods

Aluminum was routinely removed from the dissolved sludge by adding a known aliquot of sample to an equal volume of 6 to 8M NaOH. The resulting solution was centrifuged, and aliquots of the centrifugate were removed for analyses as if these were supernate samples. As a cross-check, some samples were also titrated with ethylenediaminetetraacetic acid (EDTA).

Neutron Activation Analyses (NAA)

The 15-mg ^{252}Cf neutron activation facility (Figure 4), was used to determine sodium and manganese by the technique of automated absolute activation analyses.[21] Analysis by neutron activation was somewhat complicated because the samples themselves gave a background of about 10^{11} dis/(min-mL), mainly from ^{137}Cs. When possible, the cesium was removed; in other cases, dilution was effective in reducing the gamma activity.

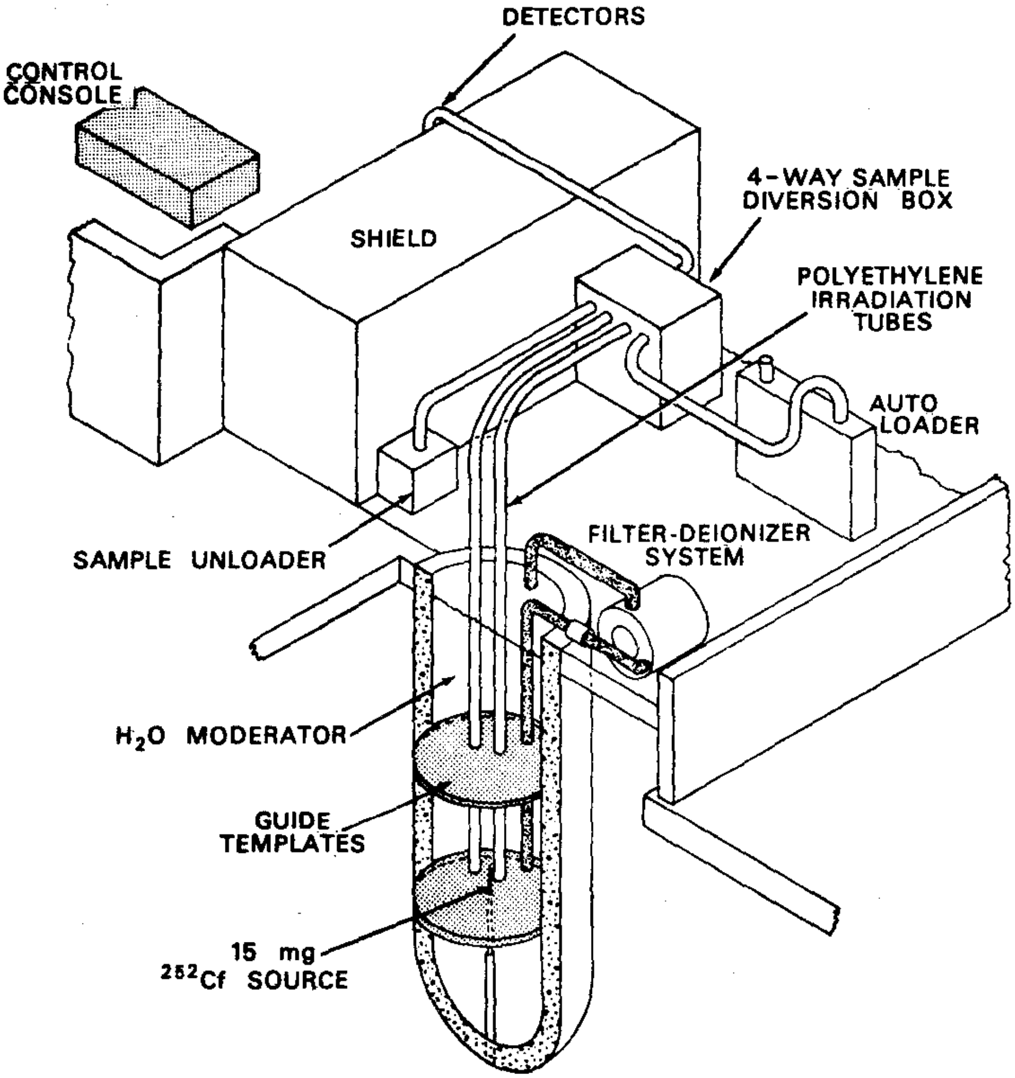

FIGURE 4. ^{252}Cf Neutron Activation Analysis Facility

Samples are moved through the rapid transport system for background counting, irradiation, and post-irradiation counting. If desired, a sample may then be ejected from the system or cycled up to 99 times through irradiation and counting. Delays can be programmed to allow very-short-lived isotopes to decay before counting. The gamma ray spectrum is then placed on magnetic tape for computer analysis. Peaks are identified and compared to those reported in the gamma ray catalog compiled by K. W. MacMurdo and W. W. Bowman.[22]

In acid solutions where ^{137}Cs removed was not effective, neutron activation with the 15-mg ^{252}Cf source offered no real advantage over atomic absorption, with the exception of manganese determination. Neutron activation analysis did, however, provide a cross-check for sodium. The dilution necessary to reduce the counter dead-time (due to ^{137}Cs) to a useful level also reduced the concentration of the major elements (such as mercury, aluminum, and iron) below the detectable limits.

Insoluble Residues

Not all sludge samples dissolve completely in constant boiling HCl. The remaining residue may vary from less than 0.1 to more than 40 wt %. These residues were analyzed by SSMS before any further analyses were attempted. The very small residues usually contained only silicon, oxygen, and/or aluminum in significant quantities. For the higher weight residues, SSMS showed the major elements to be combinations of carbon, aluminum, silicon, and oxygen. Traces of other elements were also found by SSMS, but not in amounts that would significantly effect the overall analyses of sludge.

Carbon

Weighed samples of residues for which carbon was indicated by SSMS were placed in the combustion train of a commercial carbon-hydrogen-nitrogen analyzer, and the carbon was quantitatively converted to carbon dioxide for separation and analyses by gas chromatography.

Alumina

Residues which contained both carbon and aluminum were first heated to 500°C in air to burn off the carbon. The remaining sample was fused with potassium persulfate, diluted to a known volume, and the aluminum concentration was determined by atomic absorption.

Silica

Residues which contained both carbon and silicon were first heated to 500°C in air to burn off the carbon. A solution of mixed sulfuric and hydrofluoric acids was added to the remaining residue, and the sample was heated to fume the sulfur dioxide. The burning was repeated and the weight of silicon dioxide lost [$SiO_2 + 4HF \xrightarrow{heat} SiF_{4(g)} + 2H_2O_{(g)}$] was determined.

Radionuclide Analyses

The specific activities of radionuclides in supernates, interstitial solutions, leach solutions, and totally dissolved sludge were determined by high-resolution gamma-ray spectroscopy, gross alpha counting, alpha PHA, and liquid scintillation counting. All the major fission products were sought except ^{147}Pm (a beta emitter), which was not determined.

As expected, ^{90}Sr was the principal radioactivity in the washed sludges. Other radionuclides present in significant quantities were the fission products ^{144}Ce, ^{106}Ru, and ^{154}Eu. Most of the ^{137}Cs in the raw sludges was washed out, but a residual quantity (∿3 to 12% of the original) appeared to be fixed in the product sludges. The only alpha emitters detected by alpha pulse-height analysis were ^{238}Pu, ^{239}Pu, and ^{244}Cm. The alpha radioactivity was small in every case.

Again, as expected, ^{137}Cs was the principal source of radioactivity in the supernate, interstitial solutions, and leach solutions. Other radionuclides present in significant quantities were the fission products ^{134}Cs, ^{103}Ru, and ^{106}Ru.

High-Resolution Gamma-Ray Spectroscopy

For the supernates, interstitial solutions, and leach solutions, ^{134}Cs and ^{137}Cs were measured directly (after dilution when necessary) by gamma PHA. As these two isotopes contributed more than 80% of the gamma activity, the statistics of the lesser nuclides were poor. The statistics of these nuclides were greatly improved after removal of the cesium isotopes in a zeolite column pretreated with a synthetic waste solution.

Absorption of cesium by the chosen zeolite (*Linde*® AW-500, Union Carbide Corp., New York, NY) only occurred in basic solution. Because the dissolution of both raw and pre-washed sludge required acid solutions, cesium removal from the total dissolution solutions of both raw and pre-washed sludge was ineffective. As a result, the counting statistics of the lesser gamma-emitting nuclides for the raw sludge samples were poor; only "less than" values could be obtained for most nuclides. In the pre-washing steps, however, at least 88% of the total cesium isotopes was removed. The counting statistics for the lesser nuclides on samples of pre-washed sludge were such that actual concentrations could be calculated.

Gross Alpha and Alpha Pulse-Height Analyses

Supernates, interstitial solutions, and leach solutions were diluted and standard alpha mounts were prepared for gross-alpha counting. Due to the large salt content, the statistics on these mounts were poor, but did yield sufficient precision for most determinations. Actinide separation methods are currently being investigated to develop a technique for obtaining more accurate alpha counting data. In general, the alpha activities in these solutions were too low for alpha PHA.

Dissolved sludges were diluted and standard alpha mounts[23] were prepared for gross-alpha counting with one exception. Pipets were rinsed with dilute HCl instead of dilute nitric acid. In general, the stainless steel plates were clean enough (free of evaporated deposits) to give good statistics and to give good alpha-PHA spectra.

If the plates were not clean enough to give reproducible results, both aluminum and iron were removed by the following procedure. Aluminum was first removed by precipitation and redissolution of aluminum ions with NaOH. The precipitate was centrifuged and the Na^+-$Al(OH)_4^-$-OH^- solution was discarded. The precipitate was dissolved in 8 to 10M HCl and the ferric ions were removed by repeated extraction with diethyl ether. The remaining solution was evaporated to near dryness, dissolved in nitric acid and evaporated again to near dryness. The residue was then dissolved in nitric acid, diluted to volume in a flask, and standard mounts were prepared.

^{90}Sr Analyses

^{90}Sr analyses were performed by removing the ^{90}Y from the sample. After the ^{90}Y was permitted to grow-in for about 3 days, ^{90}Y was again removed from the solution and counted by liquid scintillation techniques. For recovery yields, a standard was carried through the same procedures. ^{90}Sr was then calculated from the daughter ^{90}Y results.[24]

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APPENDIX A: SUMMARY OF SRP WASTE TANK COMPOSITIONS

The majority of the high level waste at the Savannah River Plant (SRP) consists of byproducts of the Purex (principal separations process in F Area) and the HM (principal separations process in H Area) processes. The Purex process is used to recover plutonium and uranium from irradiated, aluminum-clad, natural uranium oxide slugs. The HM process recovers neptunium and enriched uranium from aluminum-clad, uranium-aluminum fuel tubes. Other recovery processes have also been used in both areas for the separations of other isotopes.

The waste tanks contain gelatinous sludge layers that occupy about 10% of the total waste volume and have settled from alkaline supernate waste solutions. The sludge component consists of about 50 wt % water; about 15 wt % hydrous oxides or hydroxides of stable metals (Mn, Fe, Al, Hg, U, Ca, and Ni are the major metals); about 35 wt % coprecipitated or occluded salts (Table A-1); small amounts of Th, Np, Pu, Am, and Cm; and essentially all of the long-lived fission products (except cesium) originally in the irradiated fuel. The supernate contains various water-soluble salts (Table A-1) and most of the cesium radioisotopes.

The complexed aluminum ion concentration of H-Area waste is typically higher than that in F-Area waste because in the HM process, both the aluminum cladding and the cores of aluminum-uranium fuel tubes are dissolved. Aluminum nitrate is then used as the salting agent in the HM process to enhance the extraction of uranium and neptunium. The aluminum ion concentration is less in the Purex waste because the only source is the cladding material.

The sodium, hydroxide, and nitrate ions originate primarily from nitric acid recovery operations and from the NaOH added to make both the Purex and the HM process wastes basic. Although nitrite ion was occasionally added to the waste in the past during nitric acid recovery, this added nitrite is unstable in acid solutions and is oxidized to the nitrate ion. The nitrite ions found in the wastes after neutralization are produced by radiolysis during waste storage.

TABLE A-1

Chemical Composition of Waste

Constituent	*Concentration, M*	*Constituent*	*Concentration, M*
$NaNO_3$	2.2	MnO_2	0.02
$NaNO_2$	1.1	NaF	0.02
$NaAlO_2$	0.8	Na_3PO_4	0.01
NaOH	0.5	NaCl	0.01
Na_2CO_3	0.3	KNO_3	0.01
Na_2SO_4	0.3	$CaCO_3$[a]	0.006
$Fe(OH)_3$[a]	0.15	HgO[a]	0.002
		$Mg(OH)_2$	0.001
		NaI	0.0002

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[a] Predominantly in the sludge; other constituents are predominantly in the supernate.

The carbonate ion in both areas arises from three sources: (1) radiation-induced degradation of gelatin added to aid in silica removal, (2) radiation-induced degradation of dissolved TBP (tri-n-butyl phosphate) and entrained n-paraffin diluent from the solvent extraction processes, and (3) absorption of carbon dioxide from air constantly being circulated over the waste supernate in the liquid waste storage tanks to prevent buildup of radiolytically produced hydrogen. The phosphate ions also result from radiolytic degradation of TBP.

Elemental carbon, in the form of graphite, has been identified in Tank 7. It is presumed this resulted from accidental transfer of activated charcoal to the waste tank.

The sulfate ion in waste from both F and H Areas comes from the ferrous sulfamate and hydroxylamine sulfate used for valence adjustment in the Purex and HM processes. The ammonium ion is due to the hydrolysis of the sulfamate from the solvent extraction cycles in both areas and from ferrous sulfamate and hydrazine used in the ^{237}Np-^{238}Pu separation process. Ammonia is also an impurity in the purchased 64% nitric acid and the purchased ferrous sulfamate.

The primary source of iron is the ferrous sulfamate used for valence adjustment in both areas. Corrosion of the stainless steel components in the process and waste handling systems is a secondary source of iron for both areas. An additional secondary source of iron for H-Area waste is the occasional electrolytic dissolution of fuel clad in stainless steel.

Corrosion of stainless steel components and the occasional electrolytic dissolution of stainless steel clad fuel are also the main sources of chromium in the waste.

Mercury concentrations in H-Area wastes are typically higher than in F-Area wastes because the HM process uses mercuric ion as a catalyst to dissolve both the cladding and core of aluminum-uranium fuel tubes. Mercuric ion has also been added to dissolver vessels in F Area to catalyze the dissolution of aluminum-plutonium target tubes.

Nickel concentrations in F-Area waste are typically higher than in H-Area waste because a nickel coating is applied to the natural U_3O_8 slugs before they are clad with aluminum. Corrosion of the stainless steel components in the process and waste handling systems is a secondary source of nickel in both areas. An additional secondary source of nickel in H-Area waste is the occasional electrolytic dissolution of fuel clad in stainless steel.

The most important source of chloride ion in the waste is an impurity in the NaOH added to neutralize acidic waste. Secondary sources of chloride ion in some waste tanks are the special small-scale, separation processes such as the Tramex process which uses LiCl as a salting agent in the recovery of americium and curium.

A primary source of manganese and potassium in both F- and H-Area wastes is the manganese nitrate and potassium permanganate for head-end treatment. An additional source of potassium is the KF used as a source of fluoride ion in dissolver solutions. Fluoride ion is also added to precipitate plutonium in the plutonium finishing process. Upon recovery of the residual plutonium from the slag-and-crucibles, all the soluble fluoride ion is transferred to the waste tanks.

Silver is used in the dissolver off-gas scrubber systems for removal of radioactive iodine isotopes. The majority of the silver, however, is fission-product silver.

Calcium is added to the bomb-reduction system to reduce mixed PuO_2-PuF_4 to plutonium metal. The bomb-reduction crucibles are made of magnesia. Silicon is an impurity in these crucibles and is also a component part of the aluminum alloys that clad the fuel the fuel and target assemblies. Another source of silicon arises from the neutron activation of the aluminum in the jackets and cores of the fuel.

The actinides (Th, U, Np, Pu, Am, and Cm) result from losses in the recovery processes. An additional source of ^{241}Am is the clean-up of aged plutonium.

A number of elements are present because they are ^{235}U thermal fission products (e.g., Sr, Y, Zr, Nb, Mo, Ru, Rh, Ag, Cd, Zr, Nb, Sb, I, Cs, Lu, La, Ce, Pr, Nd, Pm, Sm, and Eu). The light lanthanides were also used to test the Tramex process. Hence a large amount of stable lanthanides are found in Tank 7.

Lead is used as a lubricant on all coextruded fuel tubes. Both cadmium and boron have been used as neutron poisons for nuclear safety control in both areas. The primary source of ^{60}Co is believed to be from leaking ^{60}Co sources prepared in SRP reactors.

Minor alloying elements present in the aluminum alloys used as cladding materials are copper, manganese, zinc, iron, and silicon, with trace levels of titanium and uranium present.

APPENDIX B: HANDBOOK OF SRP PROCEDURES FOR ANALYZING RADIOACTIVE LIQUID WASTES

FOREWORD

This Handbook was compiled for the analysts of the Analytical Chemistry Division, Savannah River Laboratory, operated by E. I. du Pont de Nemours and Co. for the United States Department of Energy. This Handbook contains primarily methods for analyzing radioactive waste tank sludges, salts, and supernates.

Some of the analytical procedures were developed by others; although many of these were modified to some degree. However, many of the analytical procedures were developed by personnel of the Analytical Chemistry Division by reference to existing publications, personal communications, and laboratory research. Elements are susceptible to analysis by more than one technique depending on source, original matrix, dissolution matrix, concentration, radiation levels, and other factors. This Handbook also contains alternate methods for analyses that are employed as circumstance demands. Each of these procedures was checked with the analyst performing the analysis so that the procedure is accurately described as performed.

The authors have attempted to present all of the procedures in a simple and concise manner, but in sufficient detail to make them readily usable by a chemist, but not necessarily in sufficient detail for an analyst. It is assumed the worker is familiar with the safety precautions of good laboratory techniques and with safety precautions necessary for handling radioactive samples. Before use, the safety aspects of the procedures should be reviewed by the chemist in light of his own needs and situation. References and acknowledgments are given in individual sections along with procedures for further study, if desired. It is not inferred that the procedures in this compilation are universal for any type of sample, but they have been found to be very reliable for the types of samples mentioned. The authors will welcome inquiry for clarification of any part of this compilation. It is the desire of the authors, staff, and management of the Savannah River Laboratory that this compilation will be of use and service to others.

CONTENTS

INTRODUCTION

Liquid radioactive wastes are produced at SRP primarily from nuclear fuel reprocessing operations in the two separations areas. Acidic wastes are neutralized before transfer to storage in large, underground, carbon-steel tanks.

Recovery processes in the hot and warm canyons generate waste streams that contain most of the fission products. Those waste streams that come from the warm canyon are referred to as low-activity waste (LAW). This terminology is used to identify the source of the waste and to indicate that it will not require auxiliary heat removal, as does high-activity waste (HAW).

The high-activity waste from the canyon is received in a cooled HAW tank that has secondary containment. Fresh waste is aged for at least a year to permit decay of short-lived fission products. During this period, insoluble material settles to form a layer of sludge at the bottom of the tank. The sludge is a mixture of about 50 wt % water; ∿15 wt % oxides and hydroxides of manganese, iron, aluminum, and mercury; ∿35 wt % coprecipitated or occluded soluble salts (Table B-1); small amounts of thorium, uranium, neptunium, plutonium, americium, and curium; and essentially all of the fission products originally in the irradiated fuel except cesium. After aging, the supernate, containing dissolved salts and radioactive cesium, is transferred to a continuous evaporator. Currently, the condensate from the evaporator is passed through an ion exchange column for removal of entrained cesium and then discharged to a seepage basin. When the process waste contains mercury, the condensate is also passed through a mercury trap upstream of the cesium removal column. The condensate from the evaporator is transferred to a cooled waste tank where the suspended salts settle. Upon cooling, additional salt crystallizes. This process continues until the liquid is converted to crystallized salt cake.

The low-activity waste is handled similarly to high-activity waste. Low activity salts are now being accumulated in uncooled waste tanks.

The distinction between high- and low-activity waste at the Savannah River Plant has almost vanished because of mixing from transfers of waste from one tank to another. Ranges of chemical compositions of major elements and ions in wastes are outlined in Figure B-1. The principal radioactive constituents in wastes are outlined in Figure B-2.

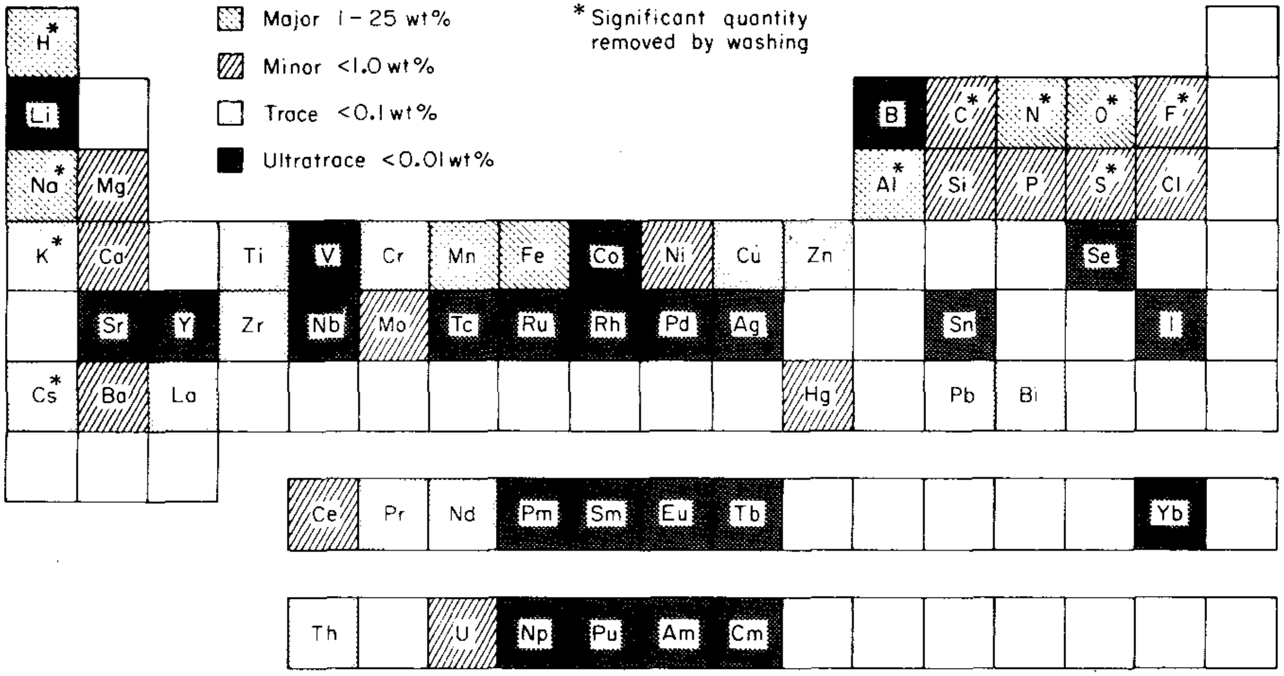

FIGURE B-1. Elements Present in Sludge

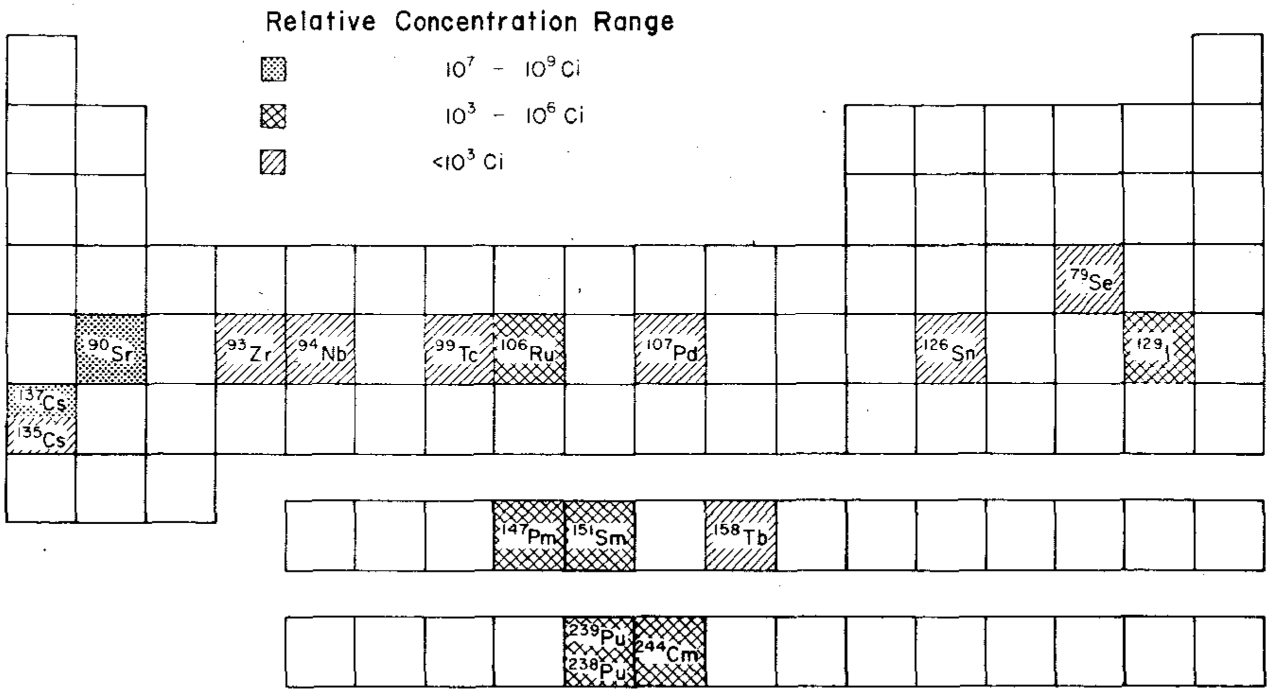

FIGURE B-2. Relative Concentration of Radionuclides

The initial handling of the sludge samples consists of drying and either total dissolution or leaching of soluble salts. All insoluble residues are dried and weighed before a portion is submitted for SSMS analysis. Most samples show only silica as the major constituent (>90%) of the residue. If the insoluble residue comprises more than 5% of the total sample, SSMS results are used as guidance to the type of analyses required. Possible dissolution procedures may be necessary. In SRP waste tanks, the insoluble residues comprise a combination of charcoal, silica, and alumina.

DRYING OF WASTE TANK SLUDGE

Introduction

Because solids from the tanks consist of hydrated oxides and hydroxides of elements such as iron, aluminum, manganese, and mercury, complete drying would require heating to about 1200°C. However, heating to this temperature would result in the decomposition and evolution of gases from known constituents such as sodium nitrate, sodium nitrite, and sodium carbonate. For this reason, a defined dry weight is used.

Reagents

None

Equipment

Balance

Beakers

Block for holding centrifuge tube

Centrifuge

Centrifuge tubes (graduated)

Drying oven

Graduated cylinders

Procedure

Step 1. Determine the total weight of the wet sample and transfer it to graduated centrifuge cones. Centrifuge for 1/4 to 1 hr. If centrifuged too long, the solid packs excessively and is very difficult to remove from the centrifuge cone. Record the volumes of solid phase and aqueous phase. Decant and combine the aqueous phases. Measure and record the total volume and weight of aqueous phases. Calculate and record the density of the aqueous phase. Label the aqueous phase as interstitial liquid and save for analysis.

Step 2. Combine the solid phases and measure the total weight of solids.

Step 3. Dry sample for not less than 16 hr nor more than 18 hr at 110 ±5°C. Cool in air and determine final weight. Label this sample as dried sludge.

Calculations

$$\% \text{ interstitial liquid} = \frac{\text{wt of combined aqueous phases}}{\text{total wt of sample}} \times 100$$

$$\% \text{ dried sludge} = \frac{\text{wt of dried sludge}}{\text{total wt of sample}} \times 100$$

$$\text{Density of interstitial liquid} = \frac{\text{wt of aqueous phase, g}}{\text{volume of aqueous phase, mL}}$$

$$\% \text{ sorbed water} = \frac{(\text{total wt of solids})(\text{wt of dry sludge})}{\text{total wt of solids}} \times 100$$

DISSOLUTION OF SLUDGE

Introduction

Three methods have proven to be effective sludge dissolution procedures. Each method, however, destroys the analysis of one or more desired ions. Reasonable estimates of the nitrite ion and nitrate ion concentrations can be made by successive leachings with distilled water.

The quickest and most effective method for dissolving sludge is to reflux in 6M HCl. This method does, however, have several drawbacks:

- All off-gases must be trapped, as HCl is corrosive to the stainless-steel cell-liners.
- Chloride ion is activated during neutron irradiation and therefore complicates this method of analysis.
- Analyses for chloride, nitrate, and nitrite ions and for elemental lead, mercury, and silver are not possible.

Even with these shortcomings, HCl is still the first choice for the widest range of analytical determinations.

The second effective method is to treat the sludge with 8M HNO_3 - 0.1M HF followed by evaporation to near dryness. This step is repeated several times. In general, this procedure takes much longer than HCl and requires closer attention by the analyst. However, the final solution matrix is more compatible with neutron activation, atomic absorption, and electrochemical methods of analyses. The major shortcomings are:

- Analyses for many ions, e.g., nitrate, nitrite, chloride, and fluoride anions, and for K, Si, Ba, and Ca cations are destroyed.
- Analyses for Al, Pu, Am, Cm, and Th are complicated.

The third effective method is repeated fuming with sulfuric acid. The major shortcomings here are:

- Analyses for sulfate, nitrate, nitrite, and chloride anions and Ag, Ca, Sr, Hg, Pb, and Ba cations are destroyed.
- Constant attention by the analyst is required.

DISSOLUTION OF SLUDGE WITH HCl

Introduction

The widest range of analysis can be performed when boiling 6M HCl is used to dissolve the sludge.

Reagents

Nitrogen gas
6M HCl
$\geq$6M NaOH
Distilled water

Equipment

Balance
Weighing vials
Dissolution train (Figure A-3)
Hot plate
200-mL volumetric flask

Procedure

Step 1. Weigh accurately 2 to 4 g sample of dry sludge in a weighing vial.

Step 2. Transfer total sample to dissolution flask.

Step 3. Add 100 mL of 6M HCl.

Step 4. Connect up the dissolution train.

Step 5. Start a slow flow of nitrogen gas through the train.

Step 6. Start water flow through the reflux condenser.

Step 7. Reflux the solution 1 to 6 hr.

Step 8. Cool the solution and then stop the nitrogen gas and water flows.

Step 9. Decant the solution to a 200-mL volumetric flask.

Step 10. Rinse dissolving flask with distilled water and add washings to the volumetric flask.

Step 11. Dilute to volume with distilled water.

Step 12. Remove residue from dissolving flask; dry and weigh.

Step 13. Submit residue for SSMS analysis.

Calculations

$$\% \text{ residue} = \frac{\text{wt residue}}{\text{wt sample}} \times 100$$

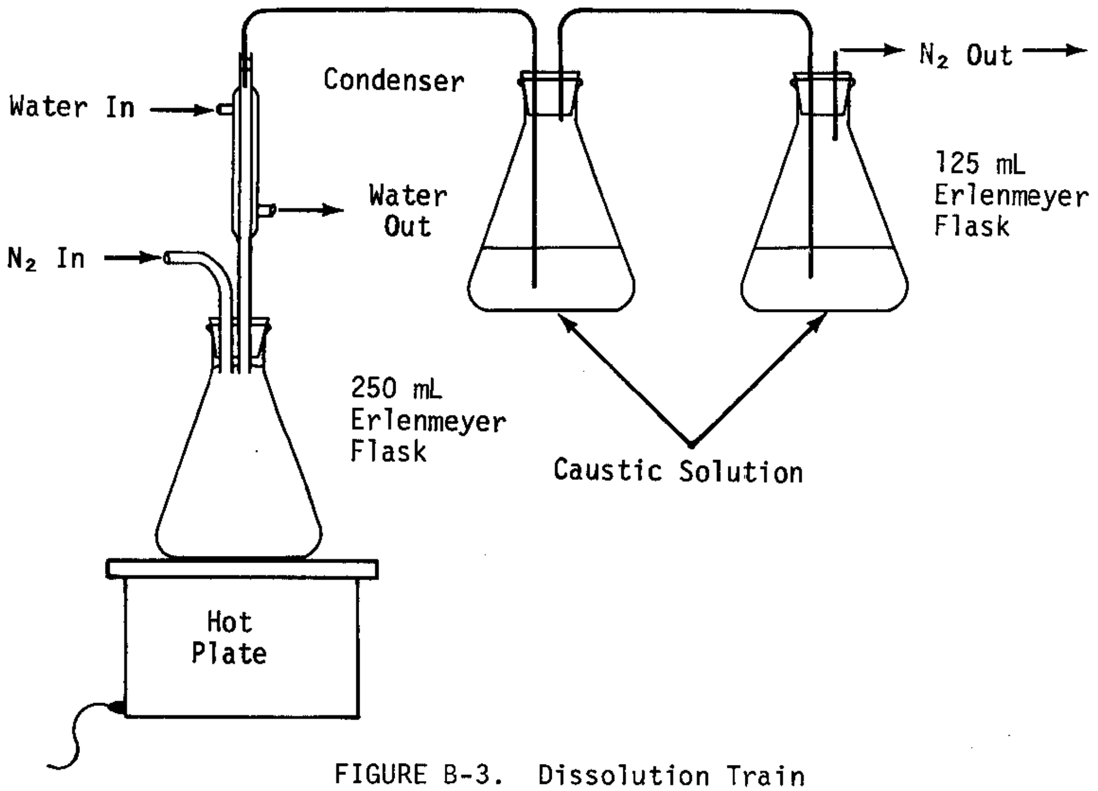

FIGURE B-3. Dissolution Train

DISSOLUTION OF SLUDGE WITH MIXED NITRIC/HF ACIDS

Introduction

The second most effective method to dissolve sludge is to evaporate to near dryness several times with an 8M nitric acid - 0.1M HF mixture.

Reagents

8M nitric acid - 0.1M HF mixed acid solution

Distilled water

Equipment

Balance

Weighing vials

Hot plate

200-mL volumetric flask

Stainless steel beaker.

Procedure

Step 1. Weigh accurately 2 to 4 g sample of dry sludge in a weighing vial.

Step 2. Transfer sample to stainless steel beaker.

Step 3. Add 100 mL of mixed acid.

Step 4. Maintain temperature at near boiling until the sample volume is reduced to about 10 mL.

Step 5. Repeat Steps 3 and 4.

Step 6. Repeat Step 5.

Step 7. Repeat Step 3. Heat to boiling. Most of the solid should dissolve. If the solid does not dissolve, repeat Step 4; if most of the solid dissolves, proceed to Step 8.

Step 8. Cool the solution and decant to a 200-mL volumetric flask.

Step 9. Rinse the beaker with distilled water and add washings to the volumetric flask.

Step 10. Dilute to volume with distilled water.

Step 11. Remove residue from beaker, dry, and weigh.

Step 12. Submit residue for SSMS analysis.

Calculations

$$\%\ \text{residue} = \frac{\text{wt residue}}{\text{wt sample}} \times 100$$

DISSOLUTION OF SLUDGE WITH SULFURIC ACID

Introduction

The third most effective method to dissolve sludge is repeated fuming with sulfuric acid.

Reagents

9M sulfuric acid

0.1M sulfuric acid

Equipment

Ceramic dish

Hot plate

200-mL volumetric flask

Balance

Weighing vials

Procedure

Step 1. Weigh accurately 2 to 4 g sample of dry sludge.

Step 2. Transfer total sample to ceramic dish.

Step 3. Add ∿25 mL of 9M sulfuric acid and slowly evaporate to dense white fumes.

Step 4. Repeat Step 3 at least three times.

Step 5. Add about 100 mL of 0.1M sulfuric acid and heat to near boiling. If most of the solid dissolves, proceed to Step 6; if the solid does not dissolve, evaporate to ∿10 mL and repeat Step 3.

Step 6. Decant the solution to a 200-mL volumetric flask.

Step 7. Rinse dissolving dish with distilled water and add washings to the volumetric flask.

Step 8. Dilute to volume with 0.1M sulfuric acid.

Step 9. Remove residue from dissolving flask, dry, and weigh.

Step 10. Submit residue for SSMS analysis.

Calculations

$$\% \text{ residue} = \frac{\text{wt residue}}{\text{wt sample}} \times 100$$

LEACHING SOLUBLE SALTS FROM RAW DRY SLUDGE

Introduction

All effective methods of sludge dissolution prevent analyses of nitrate and nitrite. A reasonable estimate of the nitrate and nitrite concentration can be determined by first leaching them from the dried solid with distilled water followed by either Raman or colorimetric determination.

Reagents

Distilled water

Equipment

Centrifuge

Centrifuge tubes with caps

Block for holding centrifuge tubes

Vortex mixer

Balance

50 mL volumetric flask

Gamma tubes

Procedure

Step 1. Weigh accurately a 1 to 2 g sample of dry sludge in a centrifuge cone.

Step 2. Add 10 mL of distilled water.

Step 3. Agitate on a vortex mixer for not less than 30 minutes.

Step 4. Centrifuge and decant solution into a 50-mL volumetric flask.

Step 5. Repeat Steps 2, 3, and 4 three times, combining the four washings.

Step 6. Dilute the solution to the mark on the 50-mL volumetric flask with distilled water.

Step 7. Take appropriate aliquots for analysis of Na and K cations and sulfate, nitrate, and nitrite anions.

Step 8. Prepare gamma tubes for gamma-PHA and submit for analyses.

NOTES:

1. At least three washes are necessary to leach greater than 70 wt % of the soluble salts from the sludge. Excessive washings, however, result in sludge peptization.

2. Na and K are determined by atomic absorption. Normally, a dilution factor of 1000 will be necessary for Na and K.

3. Frequently, nitrate, nitrite, and sulfate anions may be determined by Raman analysis. However, sludge from some tanks fluoresce; hence, Raman analysis cannot be used. The sulfate ion concentration may be below the detection limit for Raman. If Raman analyses cannot be used, nitrate and nitrite ion concentrations are determined by colorimetric techniques, and sulfate ion concentrations are determined by turbidity methods.

ANALYTICAL TECHNIQUES

Elements and ions can be determined by a variety of techniques depending upon the type of sample, e.g., solid sludge, dissolved sludge, or leach solution. As a number of multielement techniques are available, frequently an element may be determined by more than one technique. If these results do not agree (due to interferences or analytical error), a single-element technique can resolve the difference. For all major elements, at least one secondary method will serve as a random cross-check. The following sections describe the techniques available for analyzing SRP waste tank samples.

GROSS ALPHA DETERMINATION (DIRECT MOUNT)

Introduction

Gross alpha determinations are necessary for all solutions prior to atomic absorption analysis. The gross alpha activity of a solution is determined by mounting an aliquot on a stainless steel plate (planchet), evaporating to dryness, and counting the activity on the planchet with an alpha proportional counter or an alpha scintillation counter.[1,2] The counting efficiencies of the two types of counter will be different, the proportional counter has a counting efficiency (or counting yield) close to 50%; the scintillation counter has a counting efficiency of 25 to 30%. In both cases, the counting efficiency should be monitored daily with a standard.

The mounted solution should have a low solids content (preferably less than 10 mg/mL), because solids precipitating from the solution as evaporation proceeds will absorb alpha particles and the results will be low. The corrosive effects of HCl on the metal planchet are minimized by diluting the sample with water and by rinsing the pipets with water.

The presence of beta and beta-gamma emission in gross alpha samples will affect the alpha counting rate if the beta or beta-gamma level is about 10^7 to 10^8 beta disintegrations per minute (d/m). At these levels, the beta pulses in the counter will "pile up" to a value as strong as an alpha pulse, hence spurious pulses due to beta or beta-gamma are counted and interpreted as alpha counts unless a correction is made. Generally, if the sample mount has an activity level of 20 mR/hr or above (dose rate at 3 inches) interference of beta pulses is present. The precision of the method depends on the number of counts per minute present and the time of counting. A coefficient of variation of about 1% is obtained on alpha plates containing $\sim 10^4$ counts/min when counted for 10 minutes (counting statistics only).

Reagents and Chemicals

Distilled water

Collodion solution, 0.5 mg solids/mL

Equipment

- Forceps, 4-in. long
- Stainless steel dishes
- Stainless steel planchets
- Asbestos boards
- Infrared heater
- Meeker burner
- Planchet holders
- Acrylic carrier
- Counting plate heater
- Micropipets

Procedure

Step 1. Make any necessary preliminary sample dilutions.

Step 2. Using forceps, place a clean, flat, stainless steel planchet on an asbestos board beneath an infrared heater.

Step 3. Pipet the sample aliquot to the center of the planchet.

Step 4. If a micropipet is used, rinse the pipet twice with distilled water and add the rinsings to the planchet. All of the liquid must remain on the planchet at this point.

Step 5. Turn on the infrared heater and evaporate the solution on the planchet to dryness.

Step 6. Using a Meeker burner, flame the planchet to a dull red heat. Allow the planchet to cool on asbestos board.

Step 7. Add 3 drops of collodion solution to the planchet and allow the collodion to spread over the surface.

Step 8. After the planchet has air-dried for 5 minutes, place on marked planchet holder and deliver to the counting room in an acrylic carrier.

Calculation

$$\text{Alpha disintegrations/minute/mL} = \frac{A \times C \times E}{B \times D \times F}$$

where

A = alpha disintegrations/minute

B = volume of original sample taken for dilution, mL

C = volume to which original sample was diluted, mL

D = aliquot of diluted sample taken for analysis (or for second dilution), mL

E = volume to which D was diluted, mL

F = aliquot (from E) taken for analysis, mL

References

1. B. F. Rider. *Selected Analytical Methods for Purex Process Control.* USAEC Report KAPL-890, General Electric Corp., Knolls Atomic Power Laboratory, Schenectady, N.Y. (1954).

2. C. J. Rodden. *Analytical Chemistry of the Manhattan Project.* McGraw-Hill, New York, N.Y. (1950). P. 665f.

GROSS BETA-GAMMA DETERMINATION (DIRECT MOUNT)

Introduction

Gross beta-gamma determinations are necessary for all solutions prior to atomic absorption analysis. The gross beta-gamma activity of a solution is determined by mounting an aliquot on a stainless steel plate (planchet) evaporating to dryness, and counting the activity on the planchet with a sodium iodide scintillation counter.[1,2] As the waste being analyzed is normally very old, the beta-activity is assumed to be about the same as the measured gamma activity.

The corrosive effects of the HCl on the metal planchet are minimized by diluting the sample with water and by rinsing the pipets with water.

Reagents and Chemicals

Distilled water

Collodion solution, 0.5 mg solids/mL

Equipment

Forceps, 4-in. long

Stainless steel dishes

Stainless steel planchets

Asbestos boards

Infrared heater

Meker burner

Planchet holders

Acrylic carrier

Counting plate heater

Micropipets

Procedure

Step 1. Make any necessary preliminary sample dilutions.

Step 2. Using forceps, place a clean, flat, stainless steel planchet on an asbestos board beneath an infrared heater.

Step 3. Pipet the sample aliquot to the center of the planchet.

Step 4. If a micropipet is used, rinse the pipet twice with distilled water and add the rinsings to the planchet. All of the liquid must remain on the planchet at this point.

Step 5. Turn on the infrared heater and evaporate the solution on the planchet to dryness.

Step 6. Using a Meker burner, flame the planchet to a dull red heat. Allow the planchet to cool on asbestos board.

Step 7. Add 3 drops of collodion solution to the planchet and allow the collodion to spread over the surface.

Step 8. After the planchet has air-dried for 5 minutes, place on marked planchet holder and deliver to the counting room in an acrylic carrier.

Calculation

$$\text{Gamma counts/minute/mL} = \frac{A \times C \times E}{B \times D \times F}$$

where

A = gamma counts/minute

B = volume of original sample taken for dilution, mL

C = volume to which original sample aliquot was diluted, mL

D = aliquot of diluted sample taken for analysis (or for second dilution), mL

E = volume to which D was diluted, mL

F = aliquot (from E) taken for analysis, mL

References

1. B. F. Rider. *Selected Analytical Methods for Purex Process Control.* USAEC Report KAPL-890, General Electric Corp., Knolls Atomic Power Laboratory, Schenectady, N.Y. (1954).

2. C. J. Rodden. *Analytical Chemistry of the Manhattan Project.* McGraw-Hill, New York, N.Y. (1950). P. 665f.

ALPHA SPECTROSCOPY (ALPHA-PHA)

Introduction

Alpha spectroscopy (alpha-PHA) is used to determine plutonium and curium content of the SRP waste tank samples.[1,2] The same planchets for gross alpha determinations are counted in the alpha-PHA counters.

Reagents and Chemicals

Distilled water

Equipment

See gross alpha procedure.

Procedure

See gross alpha procedure.

Calculations

See gross alpha procedure.

References

1. *Laboratory Manual A, Semiconductor Detectors and Associated Electronics*. Ortec, Inc., Oak Ridge, Tenn. (1968).
2. Kai Seigbahn, Ed. *Alpha, Beta- and Gamma-Ray Spectroscopy*. Vol. 1, North-Holland Publishers Co., Amsterdam (1965).

BETA SPECTROSCOPY

Introduction

Only one isotope, ^{90}Sr, is determined by beta spectroscopy. The ^{90}Sr is precipitated along with a strontium carrier solution. The ^{90}Y daughters are counted directly and the results are compared with a standard carried through the sample procedure.

Reagents and Chemicals

Ammonium persulfate, 0.1M

Fuming nitric acid

Potassium carbonate solution, 5M

Strontium carrier solution, 0.1M

Equipment

Centrifuge

Centrifuge cones

Procedure

Step 1. To an aliquot of sample, add 1 mL of 0.1M strontium carrier.

Step 2. Adjust to about 0.1N acid or less and make about 0.1M ammonium persulfate.

Step 3. Heat in boiling water for about 10 to 60 minutes - a white precipitate will form.

Step 4. Centrifuge and discard supernate. Wash precipitate with water, centrifuge, and discard wash.

Step 5. Add about 10 drops of 5M potassium carbonate, heat, then add water to 40 mL. Centrifuge and discard supernate.

Step 6. Dissolve precipitate with 3 to 4 drops of fuming nitric acid.

Step 7. Repeat precipitation if needed (water, persulfate, etc.).

Step 8. Dilute the nitric acid solution to known volume.

Step 9. Wait 4 days.

Step 10. Count the ^{90}Y daughter by beta spectroscopy.

Calculations

Compare counts to a standard carried through the same procedure.

Notes

Carry a standard through the same procedure as the samples.

References

1. M. A. Barkouskie. "Liquid Scintillation Counting." *American Laboratory 8* (5), 101 (1976).
2. D. L. Harrocks. *Application of Liquid Scintillation Counting*. Academic Press, New York, N.Y. (1974).

GAMMA SPECTROSCOPY (GAMMA-PHA)

Introduction

Gamma pulse height analyses (gamma-PHA) are usually made for the following elements which are normally present in SRP waste tanks:

- Americium
- Antimony
- Cerium
- Cesium
- Cobalt
- Curium
- Iodine
- Niobium
- Palladium
- Promethium
- Ruthenium
- Samarium
- Selenium
- Technetium
- Tin
- Zirconium

Reagents and Chemicals

1M nitric acid

Equipment

- Gamma-PHA sample vials
- Ice cream cartons
- Polystyrene vials
- Tape

Procedure

Step 1. Transfer into the gloved box or radiobench, by means of a small ice cream carton, the pulse height sample vial (8 mL glass, black plastic cap).

Step 2. Remove the top from the sample container by means of tongs or a disposable decapper.

Step 3. Pipet into the glass vial a sample aliquot containing an estimated 10^4 to 10^8 gamma counts/minute. Use $\sim$1M HNO_3 for rinsing the pipet.

Step 4. Dilute the solution in the glass vial to the 4-mL mark with ∿1M HNO_3. By means of tweezers, stopper the vial tightly with its plastic cap. NOTE: All the samples should be diluted to 4 mL so that results of analysis of a series of samples, or different samples, will all be on the same basis. Organic samples are diluted to 4 mL with diethylbenzene. It may be more convenient to add a fixed volume of 1M HNO_3 or diethylbenzene before passing the sample into the containment facility so that when the sample is pipetted, a total volume of 4 mL is obtained.

Step 5. Transfer the ice cream carton containing the glass vial to the entry port connecting the gloved box to a hood or radiobench.

Step 6. Now, working in the hood or radiobench, transfer, by means of tongs, the glass vial from the ice cream carton in the entry port into a clean polystyrene vial. At this stage, take special precautions to keep the polystyrene vial clean on the outside. Cap the polystyrene vial with its plastic "press fit" cap. Check contamination level of the outer vial with a smear paper. Tape the cap to the vial. Label the outside vial.

Step 7. Transport the vial to the counting room for pulse height analysis.

Calculations

All calculations are made with a computer code.[1-3]

References

1. W. W. Bowman and K. W. MacMurdo. *Atomic and Nuclear Data Tables.* Vol. 13, pp 89-292 (1974).

2. R. V. Slates. *GELI 2 and SPAN 2.* USAEC Report DP-1275, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S.C. (1971).

3. W. W. Bowman. "Rapid Analysis of Germanium Spectra." *Nuclear Instruments and Methods 96,* 135 (1971).

SPARK-SOURCE MASS SPECTROGRAPHIC ANALYSIS (SSMS)

Introduction

A general elemental analysis of most samples is performed with a spark-source mass spectrograph. Solid samples are loaded directly on a gold electrode for sparking. Acid samples and most leach samples are spiked with indium and then dried, a drop at a time, on a gold electrode. Samples very high in sodium salts, such as the supernate, interstitial liquid, and the first leach solution, are usually diluted by a factor of 10 to 100 and spiked with indium before loading onto the gold electrode as above (better spark characteristics and more consistent results are obtained by this technique). Samples that were washed to remove most of the ^{137}Cs-^{134}Cs gamma radiation, are ground with graphite and pressed into an electrode.

Reagents

Spike solution containing indium

Graphite

Equipment

Gold electrodes

Press to prepare graphite electrodes

SSMS instrument

Procedure for Solids

Step 1. Load a gold electrode with solid sample by normal procedure.

Step 2. Transfer the loaded electrode into the SSMS glove box and position it in the SSMS instrument.

Step 3. Spark the sample by normal procedure; develop and read the plate by normal procedure.

Step 4. Report elements present as wt %.

Procedure for Solutions

Step 1. Add an aliquot of sample to a volumetric flask.

Step 2. Add an aliquot of indium spike solution to the volumetric flask.

Step 3. Dilute to volume.

Step 4. Add solution to a gold electrode and dry, one drop at a time.

Step 5. Transfer the loaded electrode into the SSMS glove box and position it in the SSMS instrument.

Step 6. Spark the sample by normal procedure; develop and read the plate by normal procedures.

Step 7. Report elements present in ppm units for the undiluted sample.

Procedure for Solids in Graphite

Step 1. Grind a weighed amount of sample with a weighed amount of graphite.

Step 2. Press into an electrode.

Step 3. Transfer this electrode into the SSMS glove box position it in the SSMS instrument.

Step 4. Spark the sample by normal procedures; develop and read the plate by normal procedure.

Calculations

$$\text{wt \% of element} = \frac{\text{ppm} \times 10^{-6} \times \text{ total volume of sample, mL}}{\text{total weight of sample, g}} \times 100$$

Reference

1. A. J. Ahearn, Ed. *Mass Spectrometric Analyses of Solids.* Elsevier Publishing Co., New York, N.Y. (1966).

MULTIELEMENT ANALYSIS BY ABSOLUTE NEUTRON ACTIVATION ANALYSIS (NAA)

Introduction

The concentration of some of the major elements in SRP waste, e.g., Na, Fe, and Mn, are often determined by absolute neutron activation analysis. As the samples are usually high in ^{137}Cs gamma activity, the samples must be diluted by a factor of 10^6 before activation. For this reason, only major element analyses are attempted.

Cross-checks indicate this method to have an accuracy of about ±10%.

Reagents and Chemicals

0.1M nitric acid

Equipment

Volumetric flasks

Micropipets

NAA rabbits and inner vials

Procedure

Step 1. Dilute the sample by successive dilutions by a factor of 10^6.

Step 2. Pipet 10 mL of the diluted solution into a plastic vial. Tape cap.

Step 3. Transfer the plastic vial into a clean NAA rabbit; at this stage take special precautions to keep the rabbit clean on the outside.

Step 4. Label vial and transport the sample to the NAA laboratory for activation analysis.

Calculations

All calculations are performed by a computer code.[1-5]

References

1. K. W. MacMurdo and W. W. Bowman. *Automated Absolute Activation Analysis with Large* ^{252}*Cf Sources*. USDOE Report DP-1457, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S.C. (1978).

2. W. W. Bowman and K. W. MacMurdo. *Atomic and Nuclear Data Tables*. Vol. 13, Nos. 2-3 (1974).

3. N. E. Holden and F. W. Walker. *Chart of Nuclides*. 11th Ed. General Electric Corp., Knolls Atomic Power Laboratory, Schenectady, N.Y. (1972).

4. J. M. A. Lenihan and S. J. Thompson, Eds. *Advances in Activation Analysis*. Vol. 1, Academic Press, New York, N.Y. (1969).

5. J. M. A. Lenihan, S. J. Thompson, and V. P. Guinn, Eds. *Advances in Activation Analysis*. Vol. 2, Academic Press, New York, N.Y. (1972).

DELAYED NEUTRON COUNTING

Introduction

Total fissile content of the dissolved solids is determined by delayed neutron counting. As uranium is the major fissile element, this is paramount to a uranium analysis.[1-3]

Reagents and Chemicals

0.1M nitric acid

Equipment

Pipets

Micropipets

Volumetric flask

NAA rabbits and inner vials

Procedure

Prepare a sample similar to one prepared for multielement analysis by absolute neutron activation analysis.

Calculations

All calculations are performed by computer code.

References

1. K. W. MacMurdo and W. W. Bowman. *Automated Absolute Activation Analysis with Large* ^{252}*Cf Sources*. USDOE Report DP-1457, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, S.C. (1978).
2. E. K. Hyde. *The Nuclear Properties of the Heavy Elements*, Vol. III. Prentice-Hall, Inc., Englewood Cliffs, N.J. (1964).
3. K. W. MacMurdo, R. M. Harbour, and R. W. Benjamin. *J. Inorg. Nucl. Chem. 33*, 1241 (1971).

ATOMIC ABSORPTION (AA) ANALYSIS FOR VARIOUS ELEMENTS

Introduction

Atomic absorption analysis is used as a cross-check on other procedures and as the major method of analysis for many elements.[1-5] In general, a dilution of about 1000 is necessary to dilute the alpha, beta, and gamma contents of the SRP waste solutions to meet the atomic absorption laboratory limits. This dilution factor places many elements into the correct concentration range for direct AA analysis. For other analyses, additional dilution may be necessary.

Reagents and Chemicals

0.1N nitric acid

Equipment

Pipets

Micropipets

Volumetric flask

Procedure

Step 1. Mount a gross alpha-gamma planchet and measure the gross alpha and gross gamma contents.

Step 2. Calculate the minimum dilution necessary to dilute alpha and gamma below the atomic absorption laboratory limits. (Normally a factor of 1000 is sufficient.)

Step 3. Dilute an aliquot with 0.1M HNO_3 (usually 25λ to 25 mL).

Step 4. Determine the gross alpha and gross gamma on the diluted sample.

Step 5. When both the gross alpha and gross gamma are within the limits, deliver the diluted sample, the gross alpha and gamma results, and a sample request form (which gives the dilution factor of the sample for the various elements being requested) to the atomic absorption laboratory.

Step 6. The results for the various elements are reported as ppm in the original stock solution.

Step 7. Calculate the percentage of each element.

Calculations

$$\% \text{ element} = \frac{\text{ppm of element} \times \text{liters of stock solution}}{\text{mg sludge sample}} \times 100$$

References

1. A. Walsh. "Application of Atomic Absorption Spectra to Chemical Analysis." *Advances in Spectroscopy*, Vol. II. H. W. Thompson, Ed., Interscience Publishers, New York, N.Y. (1961).

2. B. V. L'vov. "The Analytical Use of Atomic Absorption Spectra." *Spectrochim. Acta 17*, 761 (1961).

3. A. C. Menzies. "A Study of Atomic Absorption Spectroscopy." *Anal. Chem. 32*, 898 (1960).

4. J. D. Winefordner and T. J. Vickers. "Flame Spectroscopy." *Anal. Chem. 46* (5), 192 R (1974).

5. J. W. Robinson. *Atomic Absorption Spectroscopy*. Marcel Dekker, New York, N.Y. (1975).

LASER-RAMAN ANALYSIS FOR ALUMINATE, CARBONATE, CHROMATE, NITRATE, NITRITE, AND SULFATE IONS

Introduction

Polyatomic anions in the supernate, interstitial, and wash or leach solutions can be determined by a laser-Raman spectrometric method.[1,2] The liquid samples are clarified by centrifugation, contained in conventional 1-mm-ID glass capillaries and sealed with *Apiezon** wax. A second aliquot of sample is spiked with perchlorate ion and contained as above. The spectra of both aliquots are obtained and the concentrations are then calculated from the peak heights.

Reagents

Perchlorate acid standard solution

Equipment

Apiezon wax

1-mm-ID capillary tubes

Centrifuge

Centrifuge tubes

Micropipets

Transfer pipets

Volumetric flask, 10 mL

Procedure

Step 1. Centrifuge sample.

Step 2. Load 1-mm-ID capillary tube.

Step 3. Seal with *Apiezon* wax.

Step 4. Transfer aliquot of sample to a 10-mL volumetric flask containing the perchlorate acid spike.

Step 5. Dilute to volume with water.

---

* Tradename of James G. Biddle Co., Plymouth Meeting, Penn.

Step 6. Load 1-mm-ID capillary tube with spiked sample.

Step 7. Seal with *Apiezon* wax.

Step 8. Check tube to make sure no contamination was transferred to the capillary tubes.

Step 9. Align sample in Raman spectrometer.

Step 10. Run spectrum of both the sample and the spiked sample.

Step 11. Calculate peak heights.

Calculations

Calculate the nitrate ion concentration from the perchlorate ion concentration in the spiked sample. Then, the nitrate ion concentration serves as an internal standard to calculate the concentrations of the other anions.

References

1. A. L. Marston. "Analysis of Radioactive Waste Supernate by Laser-Raman Spectrometry." *Nucl. Technol. 25*, 576 (1975).
2. H. H. Willard, L. L. Merritt, Jr., and J. A. Dean. *Instrumental Methods of Analysis*, 3rd ed., D. Van Nostrand Co., Inc., New York, N.Y. (1958).

X-RAY DIFFRACTION FOR SLUDGE SOLIDS

Introduction

After leaching the soluble salts from the raw sludge samples, the radiation level is reduced by dilution so that X-ray diffraction methods can be used to identify some of the remaining solids.

Reagents and Chemicals

Distilled water

Equipment

Centrifuge

Centrifuge cones

Drying oven

Procedure

Step 1. Place a portion of sample in a centrifuge cone.

Step 2. Add distilled water and mix on a vortex mixer for not less than 30 minutes.

Step 3. Centrifuge sample and pour off the water.

Step 4. Repeat Steps 2 and 3 at least twice more.

Step 5. Dry sample in oven at about 110°C for about 16 hr.

Step 6. Bag out the sample and deliver it to the X-ray diffraction lab using normal precautions.

Step 7. Run X-ray diffraction patterns using normal procedures for radioactive samples.[1-3]

References

1. H. H. Willard, L. L. Merritt, Jr., and J. A. Dean. *Instrumental Methods of Analysis,* 3rd ed., D. Van Nostrand Co., Inc., New York, N.Y. (1958).

2. B. D. Cullihy. *Elements of X-ray Diffraction*. Addison-Wesley, Publ., Reading, Mass. (1956).

3. H. P. Klug and L. E. Alexander. *X-ray Diffraction Procedures*. John Wiley and Sons, New York, N.Y. (1974).

SPECIFIC ION ELECTRODE TECHNIQUE FOR CHLORIDE ION

Introduction

Chloride ion concentration is determined for the leach solutions only by the chloride-specific ion electrode.[1]

Reagents and Chemicals

Sodium chloride, 0.10N: carefully weigh 5.844 g of dried ACS grade NaCl and dilute to 1000 mL with deionized water; store in polyethylene bottle.

Sodium nitrate, ACS grade, chloride-free.

Equipment

Magnetic stirrer and *Teflon** covered bar

Beakers, 100 mL

Pipets

Micropipets

pH meter and shorting strap

Combination chloride electrode (Orion Co.)

Procedure

A. Adjustment of Meter

1. Connect shorting strap to electrode outlets on meter; adjust the scale to 0 millivolts (mV).
2. Adjust the temperature dial to room temperature.
3. Remove the shorting strap and connect the combination chloride electrode.
4. Store the electrode tip in deionized distilled water.

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* Trademark of E. I. du Pont de Nemours & Co., Wilmington, Del.

B. *Analysis of Sample*

1. Add an aliquot of sample containing 0.005 to 0.025 mM of chloride to a 100-mL graduated beaker containing 10 mL of distilled water.
2. Dilute to ∿45 mL with water and add 5 mL concentrated sodium nitrate solution.
3. Add stirring bar and insert electrode in solution.
4. Set the meter to read ± mV, allow to stabilize about 2 minutes.
5. Turn on the expanded scale and set the dial reading to 0.9 (∿90 mV) on the right of zero (upper scale).
6. Using a microburet, carefully add 0.1M NaCl solution until the meter dial reads 0.723.
7. Record the buret reading. This is Reading No. 1.
8. Add more NaCl solution until the meter dial reads 0.545.
9. Record the buret reading. This is Reading No. 2.
10. Add a third increment of NaCl solution until the meter dial reads 0.368. This is Reading No. 3.

Calculations*

$$M_{Cl}\text{, Reading No. 1} = \frac{mL_{NaCl}\text{ (from Step 7)} \times N_{NaCl}}{\text{mL sample}}$$

$$M_{Cl}\text{, Reading No. 2} = \frac{mL_{NaCl}\text{ (from Step 9)} \times N_{NaCl}}{3 \times \text{mL sample}}$$

$$M_{Cl}\text{, Reading No. 3} = \frac{mL_{NaCl}\text{ (from Step 8)} \times N_{NaCl}}{7 \times \text{mL sample}}$$

Take the mean of the three values as the molarity of chloride.

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* $$M_{Cl} = \frac{mL_{NaCL} \times N_{NaCl}}{[(\log^{-1} \frac{\text{mV change}}{59}) - 1] \times \text{mL sample}}$$

Reference

1. *Instruction Manual: Halide Electrodes, Model 94-17* and *Instruction Sheet: Combination Chloride Electrode, Model 96-17*. Orion Research Inc., Oak Ridge, Tenn.

SPECIFIC ION ELECTRODE TECHNIQUE FOR FLUORIDE ION

Introduction

Fluoride ion concentration is determined on aqueous solutions only by the fluoride-specific ion electrode.[1-3] The fluoride ion activity electrode is a laser-type, doped, single crystal through which only fluoride ions can move. An electrical potential is developed across the crystal. Changes in potential are due only to changes in the fluoride ion activity in the sample.

Some limitations and interferences must be considered in using the electrode. The plastic body of the electrode is attacked by many solvents. Therefore, the electrode is immersed only in aqueous solutions. Cations (such as Al^{3+} and Fe^{3+}) that complex fluoride ions interfere. The addition of phosphoric acid solution minimizes much of the cation interference by forming secondary complexes. Strong acid solutions are diluted tenfold. Alkaline samples (pH above 8) must be neutralized. Anions normally do not interfere. A slow response (slowly drifting needle to right) is normal with very low fluoride ($<10^{-4}M$); but may be excessive if the crystal plastic joint traps solution or becomes dirty. If fluoride is high, the needle will drift to the left and the sample must be diluted. Temperature changes must be minimized while measurements are made.

The limit of detection is near $1 \times 10^{-6}M$ fluoride for solutions of pH 6 to 7. For better precision, an average of 3 measurements and calculations is used in this method. The precision with a standard NaF solution is estimated to be ±5%.

Reagents and Chemicals

Sodium fluoride, 0.10N: carefully weigh 4.199 g of dried ACS grade NaF and dilute to 1000 mL with deionized water; store in polyethylene bottle.

Potassium chloride solutions: saturated, store-stock.

Hydrochloric acid, conc.; F^- free, ACS grade.

Phosphoric acid conc.; F^- free (steam strip if fluoride ion is present), ACS grade.

Equipment

Magnetic stirrer and *Teflon*-covered bar
Beakers, polyethylene, 100 mL
Pipets
Microburet, 1 λ
pH meter and shorting strap
Fiber-type reference electrode, *Beckman* No. 270
Orion fluoride-ion-activity electrode

Procedure

A. *Adjustment of Meter*

1. Connect shorting strap to electrode outlets on meter and adjust scale to 0 mV.
2. Adjust the temperature dial to room temperature.
3. Remove shorting strap and connect fluoride electrode and reference electrode.
4. Store electrode tips in deionized distilled water.

B. *Analysis of Sample*

1. Add an aliquot of sample containing 0.005 to 0.025 mM of fluoride to a 100-mL graduated beaker containing 10 mL of distilled water.
2. Dilute to ∿45 mL with water and add 5 mL conc. phosphoric acid (Note 1).
3. Add stirring bar and insert electrodes in solution.
4. Set the meter to read ± mV, allow to stabilize for ∿2 minutes.
5. Turn on the expanded scale and set the dial reading at 0.9 (∿90 mV) on the right of zero (upper scale).
6. Using a microburet, carefully add 0.1M NaF solution until the meter dial reads 0.723.
7. Record the buret reading. This is Reading No. 1.

8. Add more NaF solution until the meter dial reads 0.545.

9. Record buret reading. This is Reading No. 2.

10. Add a third increment of NaF solution until the meter dial reads 0.368.

11. Record buret reading. This is Reading No. 3.

Calculations*

$$M_F\text{, Reading No. 1} = \frac{\text{mL}_{NaF}\text{ (from Step 7)} \times N_{NaF}}{\text{mL sample}}$$

$$M_F\text{, Reading No. 2} = \frac{\text{mL}_{NaF}\text{ (from Step 9)} \times N_{NaF}}{3 \times \text{mL sample}}$$

$$M_F\text{, Reading No. 3} = \frac{\text{mL}_{NaF}\text{ (from Step 11)} \times N_{NaF}}{7 \times \text{mL sample}}$$

Take the mean of the three values as the molarity of fluoride.

References

1. E. W. Baumann. "Trace Fluoride Determination with Specific Ion Electrode." *Anal. Chem. Acta, 42,* 127 (1968).

2. Orion Research Incorporated, *Instruction Manual, Fluoride Electrode Model 94-09.* Orion Research, Inc., Oak Ridge, Tenn.

3. J. J. Lingane. *Anal. Chem., 39,* 881 (1967).

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* Use steam-stripped phosphoric acid.

See References 1 and 2 for complete derivation of the formula for molarity given below.

$$M_F = \frac{\text{mL}_{NaF} \times N_{NaF}}{[(\log^{-1} \frac{\text{mV change}}{59}) - 1] \times \text{mL sample}}$$

COLORIMETRIC TECHNIQUE FOR IRON

Introduction

Iron is determined by colorimetric techniques for all dissolved sludge samples. Divalent iron reacts with 1,10-phenanthroline to form an orange-red chelate compound. This compound in solution has a maximum absorption at 510 millimicrons. In the absence of interferences, the color is directly proportional to the ferrous iron concentration over a pH range from 2 to 9. The color is stable for more than 24 hours.

In practice, iron in solution is reduced to the ferrous state with hydroxylamine hydrochloride, buffered to a pH of 3 to 5, the 1,10-phenanthroline solution is added, and the absorbance of the resulting chelate color is measured with a spectrophotometer.

Many ions will interfere if present in unfavorable ratios to the ion concentration. The references contain fairly complete information on interferences.[1-3] This method as used does not generally present interference problems.

The precision of the method, based on a total of 50 routine determinations is about 3% at the 95% confidence level.

Reagents and Chemicals

Phenanthroline solution, 1.0 g/L: weigh accurately 1.0 ±0.1 g of 1,10-phenanthroline monohydrate (Note 1) in a small beaker. Transfer quantitatively to a 1000-mL beaker. Add 600 to 800 mL of distilled water or deionized water. Heat the mixture while stirring to about 80°C, but do not boil, for 3 to 5 minutes. Cool to room temperature and transfer the solution quantitatively to a 1000-mL volumetric flask. Dilute to volume with deionized water and mix well.

Hydroxylamine hydrochloride solution, $HN_2OH \cdot HCl$, 10% by weight: Weigh 10 ±0.1 g of hydroxylamine hydrochloride. Dissolve in 90 mL of distilled water. Prepare fresh weekly.

Ammonium acetate buffer solution: Weigh 250 ±1 g of ammonium acetate ($HN_4C_2H_3O_2$) in 150 mL of distilled water. Add 700 mL of glacial acetic acid. Dilute the mixture to 1000 mL with distilled water.

Iron standard solution (Note 2), 100 μg Fe/mL: Weigh 0.1000 g of clean dry iron wire accurately. Place the weighed wire in a 1-L volumetric flask. Add 10 mL of 4M HCl and heat to dissolve wire. After complete dissolution, dilute to 1 L with water and mix.

Equipment

Beckman spectrophotometer, with blue-sensitive phototube, Model B.

Spectrophotometer cells, 5-cm path-length

Pipets

Volumetric flasks

Beakers

Magnetic stirrer-hot plate

Procedure

Step 1. Pipet 2 to 15 µg Fe solution into a 25-mL volumetric flask. If required, prepare dilutions in distilled water containing 1 drop conc. HCl.

Step 2. Pipet two standards in the range of 5 to 10 µg and also run a blank of distilled water along with samples.

Step 3. Add 3 mL of buffer solution and mix.

Step 4. Add 1 mL of $HN_2OH \cdot HCl$ and mix.

Step 5. Add 1 mL of 1,10-phenanthroline reagent and mix.

Step 6. Dilute to 25 mL with water, mix, and let stand for 30 minutes. The pH of this solution should be 3. Check with pH paper; if not approximately pH 3, contact supervision for instructions.

Step 7. Read absorbance of solution at a wavelength of 500 λ against the blank on a *Beckman* Model B spectrophotometer equipped with a blue sensitive phototube and a sensitivity position of 1. Use 5-cm cells.

Calculations

$$\text{Standard Factor} = \frac{\mu\text{g Fe in Std}}{\text{Optical Density (OD) of Std}}$$

$$M_{Fe} = \frac{\text{OD sample} \times \text{dilution factor} \times \text{standard factor}}{55.85 \times 1000}$$

Notes:

1. Phenanthroline as used in this work has the empirical formula $C_{12}H_3N_2 \cdot H_2O$.

2. Iron wire may be used to prepare this standard solution; such wire should be bright and free of rust. If necessary, it should be cleaned with fine emery paper to form a bright surface.

References

1. F. D. Snell and C. T. Snell. *Colorimetric Methods of Analysis*, 3rd ed., D. Van Nostrand Co., New York, N.Y. (1951). Pp. 314-316.

2. W. B. Fortune and M. G. Mellon. *Ind. Eng. Chem., Anal. Ed. 10*, 60 (1938).

3. H. H. Willard, L. L. Merritt, Jr., and J. A. Dean. *Instrumental Methods of Analysis*, 3rd ed., D. Van Nostrand Co., New York, N.Y. (1958).

COLORIMETRIC TECHNIQUE FOR MANGANESE

Introduction

Manganese is determined by colorimetry on random samples as a cross-check on the other methods.

Reagents

Distilled water

85% phosphoric acid

Sodium periodate

Equipment

Beakers

Volumetric flask, 100 mL

Procedure

Step 1. Pipet a sample aliquot containing 0.2 to 1.0 mg of manganese into a 50-mL beaker containing about 10 mL of water.

Step 2. Add 10 mL of 85 percent phosphoric acid to the beaker.

Step 3. Add approximately 0.5 g of sodium periodate to the beaker.

Step 4. Heat the solution in the beaker to boiling. Boil for at least 3 minutes and until all of the periodate is dissolved.

Step 5. Cool the solution.

Step 6. Quantitatively transfer the solution to a 100-mL volumetric flask and dilute to volume with distilled water.

Step 7. Stopper and invert the flask several times to mix the solution thoroughly.

Step 8. Transfer the solution to a 1-cm-long absorption cell and measure the absorbance at 525 millimicrons against a distilled water blank set at an absorbancy of "0".

Step 9. Record the data on the analytical record card for the sample.

Step 10. Using the absorbancy value from Step 8, determine the milligrams of manganese in the aliquot from the calibration curve.

Step 11. Record the milligrams of manganese for the sample aliquot on the analytical record card.

Calculations

Manganese: $$\text{mg/mL} = \frac{\text{mg Mn from curve}}{\text{sample aliquot, mL}}$$

$$\text{Molarity} = \frac{\text{mg Mn from curve}}{\text{sample aliquot, mL} \times 54.93}$$

Reference

I. M. Kolthoff and E. B. Sandell. *Textbook of Quantitative Inorganic Analysis*, 3rd ed., MacMillan Company, New York, N.Y. (1952).

COLORIMETRIC TECHNIQUE FOR NITRATE ION CONCENTRATION

Introduction

Nitrate ion concentration is determined on the leach solutions, interstitial liquid, and supernates by colorimetry. Although some nitrates are determined on the HCl dissolution solutions for sludge, the values determined for sludge are always low due to the reaction between nitrate ions and HCl.

Nitrate ions react with ferrous ammonium sulfate and sulfamic acid in the presence of 15M sulfuric acid to form red ferrous nitrosyl sulfate ($FeSO_4 \cdot NO$). This reaction is commonly known as the "brown ring" test for nitrates. The absorbance of the resulting solution is read on a spectrophotometer at a wavelength of 530 millimicrons. Nitrogen is evolved during the reaction and must be removed prior to reading.

In preliminary studies, a plot of absorbancy versus milligrams of nitrate followed Beer's law over an absorbancy range of 0.038 to 0.788. The coefficient of variation based on 39 analyses of a pure sodium nitrate standard was 0.9%.

The coefficient of variation with process samples is expected to be 3%.

Reagents and Chemicals

Ferrous ammonium sulfate, 40%. Dissolve 40 g of ferrous ammonium sulfate [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$] in a mixture of 20 mL of concentrated sulfuric acid and 80 mL of water.

Sulfamic acid, 10%. Dissolve 10 g of sulfamic acid (NH_2SO_3H) in distilled water, and dilute to 100 mL with water.

Sulfuric acid, 15M. Carefully add 850 mL of concentrated sulfuric acid to 170 mL of distilled water, mix well, and store in a 1-liter reagent bottle.

Nitrate standard solution: 2 mg NO_3^-/mL (0.2742 g pure dry $NaNO_2$/100 mL).

Equipment

1 ice bath

9 volumetric flasks, 10 mL

Assorted micropipets and volumetric pipets

Spectronic 20 spectrophotometer

Procedure

Preparation of the Standard Curve

Step 1. Place nine 10-mL volumetric flasks in an ice bath and pipet 200 microliters of sulfamic acid into each flask.

Step 2. Pipet 200 microliters of 40% ferrous ammonium sulfate into each flask, and swirl the flask to remove bubbles of nitrogen (Note 1).

Step 3. Into eight of the flasks, pipet (in duplicate) from the standard nitrate solution the following aliquots (in microliters): 100, 200, 400, and 600. Rinse the pipet with a minimum of distilled water. The ninth flask is for the reagent blank that is prepared by adding all the reagents, but omitting the samples. Swirl the flasks gently.

Step 4. With previously chilled 15M sulfuric acid, dilute each flask to 10 mL over a period of 3 to 4 minutes with continued swirling. Carry out this step with the flask immersed in an ice-water bath at all times. Add the sulfuric acid slowly (Note 2).

Step 5. Read the absorbancy of each sample against the reagent blank within 30 minutes on a spectrophotometer at a wavelength setting of 530 millimicrons, at a sensitivity setting of 1, and with a blue-sensitive phototube.

Step 6. Plot absorbancy versus mg of nitrate in the flask on rectangular-coordinate graph paper.

Analysis of Samples

Step 7. Prepare the necessary preliminary sample dilution in distilled water. The dilution should contain 0.3 to 200 mg NO_3^-/mL.

Step 8. Place a clean 10-mL volumetric flask in an ice bath. Add 200 microliters of 10% sulfamic acid and 200 microliters of 40% ferrous ammonium sulfate to the flask. Swirl the flask to remove bubbles of nitrogen.

Step 9. Pipet an aliquot of the sample dilution containing 0.3 to 1.0 mg nitrate into the 10-mL volumetric flask.

Step 10. Follow Steps 4 and 5. Record the absorbance of the sample.

Step 11. From the standard curve obtained above and absorbance of the sample, determine the mg of nitrate in the 10-mL flask.

Calculations

Normality of nitrate =

$$\frac{\text{mg of nitrate from standard curve} \times \text{dilution factor}}{62}$$

Notes

1. Bubbles of nitrogen gas in the sample, if not entirely removed by swirling, will result in high absorbancy readings.

2. Heat from the dilution of the sulfuric acid, if not controlled by use of the ice-water bath, will cause low absorbancy readings. This low absorbancy is due to the oxidation of ferrous nitrosyl sulfate by hot 15M sulfuric acid.

References

1. F. L. English. *Anal. Chem. 19,* 850 (1947).

2. F. D. Snell and C. T. Snell. *Colorimetric Methods of Analysis,* Vol. II, 3rd ed., D. Van Nostrand Co., New York, N.Y. (1953).

COLORIMETRIC TECHNIQUE FOR NITRITE ION CONCENTRATION

Introduction

Nitrite ion concentration is determined on the leach solutions, interstitial liquid, and supernates by colorimetry. Although some nitrites are determined on the HCl dissolution solutions for sludge, the values obtained for sludge are meaningless due to the reactions of nitrate and nitrite ions with the refluxing HCl solution.

Reagents and Chemicals

2M sodium acetate

Sulfanitic acid - dissolve 1.2 g of sulfanitic acid in a solution of 40 mL concentrated HCl and 140 mL of distilled water. Dilute to 200 mL.

N-(1-naphthyl)-ethylenediamine dihydrochloride - dissolve 1.20 g of the reagent in 140 mL of distilled water containing 2 mL of concentrated HCl. Dilute to 200 mL.

Sodium nitrite standard.

Equipment

Spectrophotometer and cells

Volumetric flask, 25 mL

Pipets

Procedure

Step 1. Add approximately 15 mL of distilled water to a 25-mL volumetric flask.

Step 2. Pipet a sample aliquot containing between 2 and 10 μg of nitrite.

Step 3. Add 500 microliters of sulfanitic acid reagent and let stand for 5 minutes.

Step 4. Add 500 microliters of N-(1-naphthyl)-ethylenediamine dihydrochloride reagent.

Step 5. Add 500 microliters of acetate buffer.

Step 6. Dilute to mark with distilled water and wait 15 minutes before reading on spectrophotometer.

Step 7. Read against a reagent blank that has all reagents but no sample; use a wavelength of 545 nm.

Step 8. Obtain µg nitrite from a calibration curve using sample procedure to obtain the curve.

Calculations

$$\frac{\text{mg nitrite}}{\text{mL}} = \frac{\mu\text{g nitrite from curve} \times \text{dilution factor}}{1000}$$

Reference

Methods for Chemical Analysis of Water and Wastes. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio (1971).

COLORIMETRIC TECHNIQUE FOR PHOSPHATE ION CONCENTRATION

Introduction

Phosphate is determined by colorimetry only as a cross-check on other methods.

Phosphate in dilute mineral acid solution reacts with molybdates to form molybdophosphoric acid. This acid is extractable in certain organic solvents, including 1-butanol. The extracted acid is reduced with stannous chloride to give a blue compound (having an unknown composition) usually referred to as molybdenum blue.

Silicates, arsenates, and germanates undergo similar reactions; but by adjustment of the conditions, the method can be made specific for phosphates and arsenates. The intensity of the alcoholic molybdenum blue solution is measured at 720 nm.

The extraction of molybdophosphoric acid by 1-butanol is carried out from 1N sulfuric acid because nitric acid solutions will cause more rapid fading of the color due to oxidation reactions. Molybdoarsenic acid is also extracted, but molybdosilicic and molybdogermanic acids are not extracted. No interference is expected from arsenates in process solutions. The spectrophotometer is calibrated with standards containing known concentrations of phosphate ion. Because the color fades with time, samples should be read within one hour after extraction and dilution. Blanks and standards should be read within the same interval.

Reagents and Chemicals

Phosphate standard, $\sim$1.0 g/L phosphate ion. Weigh accurately 1.43 to 1.45 g of potassium dihydrogen phosphate (KH_2PO_4), which has been previously dried at 110°C for 6 to 12 hours, and cooled in a desiccator (Note: $PO_4{}^{3-} = 0.6979 \times KH_2PO_4$). Quantitatively transfer the weighed sample to a 1-liter volumetric flask and dilute to 1-liter volume with distilled water. Calculation:

$$\text{mg } PO_4{}^{3-}/\text{mL} = \frac{0.6979 \times \text{g of } KH_2PO_4}{1000}$$

Phosphate working standard, $\sim$20 μg $PO_4{}^{3-}$/mL. Dilute 2 mL of the phosphate standard ($\sim$1.0 g $PO_4{}^{3-}$/liter = $\sim$1 mg/mL) to 100 mL with distilled water in a 100-mL volumetric flask. Prepare fresh weekly.

Ammonium molybdate, 6.25%. Weigh 62.5 g of ammonium molybdate $[(NH_4)_6 Mo_7O_{24} \cdot 4H_2O]$ on a triple-beam balance and transfer to a 1-liter beaker. Add 800 to 900 mL of distilled water and heat to 45 to 50°C while stirring. Continue heating until all the solid is dissolved. Cool to 20 to 25°C and dilute to ∿1 liter with distilled water.

Stannous chloride, $SnCl_2$, ∿15.5%. Weigh 100 g of $SnCl_2$ (or 119 g of $SnCl_2 \cdot 2H_2O$) in a 1-liter beaker. Add 200 mL of concentrated HCl and stir to dissolve. Dilute to 500 mL with concentrated HCl (Note 2).

Stannous chloride, 0.7% $SnCl_2$. Measure 7 mL of 15.5% $SnCl_2$ solution and dilute to 200 mL using 20 mL of 10N H_2SO_4 as part of the dilution volume, and the remainder as distilled water (Note 2).

Ethanol, 95%. Store-stock.

1-Butanol reagent. Measure ∿200 mL of 1-butanol into a 500-mL separatory funnel. Add ∿200 mL of 1N sulfuric acid. Put stopper in top and hold stopper in place. Shake vigorously 5 to 10 times. Let stand to allow layers to separate. Draw off lower layer (aqueous sulfuric acid) and discard. Repeat above steps three more times. Retain the washed 1-butanol as extractant.

Sulfuric acid, 10N. Measure 280 mL of concentrated sulfuric acid and pour carefully and slowly while stirring into 400 to 500 mL of distilled water. Cool to about room temperature. Dilute to ∿1 liter with distilled water.

Sulfuric acid, 1N. Measure 56 mL of concentrated sulfuric acid and add carefully and slowly to 800 to 1000 mL of distilled water. Dilute to ∿2 liters with distilled water.

Equipment

Spectrophotometer, *Beckman Model B*

Absorption cells, 5-cm path-length

Separatory funnels, 60-mL size; 500-mL size

Pipets

Flasks, volumetric, 25, 100, and 1000 mL

Beakers

Procedure

Step 1. To a 60-mL separatory funnel, add 7 mL of distilled water minus the volume of the sample aliquot, by means of a Mohr pipet. For example, if a 1-mL sample is to be used, measure 7-1 = 6 mL of distilled water (Note 1).

Step 2. Add by volumetric pipet 1.0 mL of 10N sulfuric acid. The aqueous layer should be 1N in sulfuric acid before equilibration with 1-butanol (Step 5). For this reason, adjustment of the quantity of 10N acid may be required, depending on sample acidity. Note that nitric acid interferes: 1 milliequivalent (meq) of nitric acid is tolerable; 4 meq is excessive (6% high).

Step 3. Add sample aliquot containing 6 to 12 micrograms of phosphate ion.

Step 4. Add 2.0 mL of ammonium molybdate, mix, and let stand for 5 minutes.

Step 5. Add 10 mL of 1-butanol, mix for 2 minutes, and allow to stand 1 minute. Separate layers and discard the lower (aqueous) layer.

Step 6. Add 5.0 mL of 1N sulfuric acid, mix 20 seconds, allow to stand for 1 minute, separate, and discard the lower (aqueous) layer.

Step 7. Repeat Step 6 twice.

Step 8. Add 15 mL of freshly diluted stannous chloride solution, mix 30 seconds, allow to stand for 5 minutes, separate, and discard the lower (aqueous) layer (Note 3).

Step 9. Transfer the 1-butanol solution from the separatory funnel to a 25-mL volumetric flask. Rinse the separatory funnel with small volumes (2 to 3 mL) of 95% ethanol, and add the rinsings to the volumetric flask.

Step 10. Dilute to the 25-mL mark with 95% ethanol.

Step 11. Measure the absorption in 5-cm-long cells (Sensitivity 1 at 720 nm) with a red sensitive phototube.

Step 12. Prepare a blank by way of Steps 1 through 10, but omitting Step 3.

Step 13. Measure the absorption of the blank under the same conditions as in Step 11.

Step 14. For calibrating the instrument, prepare dilutions of the standard phosphate solution (1.0 g/L) as follows:

100λ/100 mL H_2O = 1 μg $PO_4{}^{3-}$/mL

500λ/100 mL H_2O = 5 μg/mL

1.0 mL/100 mL H_2O = 10 μg/mL

2.0 mL/100 mL H_2O = 20 μg/mL

4.0 mL/100 mL H_2O = 40 μg/mL

5.0 mL/100 mL H_2O = 50 μg/mL

where λ = microliters of solution.

Step 15. Using 1-mL samples of each of the dilutions in Step 14, proceed by Steps 1 through 12 to obtain absorption readings for the entire range. Refer to calculations. Plot the data obtained as % absorption (Y axis) versus phosphate ion concentration as μg/mL (X axis) on linear graph paper.

Calculations

% absorption = sample % absorption - blank % absorption

Phosphate ion concentration as μg/mL is obtained from the calibration curve for the % absorption.

$$M_{PO_4} = \frac{\mu g/mL \text{ of phosphate} \times \text{dilution factor}}{9.5 \times 10^4}$$

Notes:

1. In a routine run prepare duplicate blanks, 300 microliters (λ) and 600λ standards (of 20 μg/mL phosphate ion) and unknown samples.

   Blank absorptions = ∿0.030 unit

   300λ standard = ∿0.235 unit

   600λ standard = ∿0.440 unit

2. The concentrated stannous chloride solution should be prepared fresh at weekly intervals. The 0.7% stannous chloride solution should be prepared fresh daily.

3. After the stannous chloride solution is added, the color should be read within 1 hour.

4. The method may be used as written for soluble phosphate. For organic or insoluble phosphate, pretreatment with concentrated nitric acid followed by perchloric acid or sulfuric acid treatment to eliminate nitrates is required. Consult with supervision for details or refer to another method.

Reference

H. H. Willard, L. L. Merritt, Jr., and J. A. Dean. *Instrumental Methods of Analysis*, 3rd ed., D. Van Nostrand Company, New York, N.Y. (1958).

COLORIMETRIC TECHNIQUE FOR SILICA

Introduction

Dissolved silica is determined on samples where the SSMS results show high silicon in the dissolved sample. Dissolved silica reacts with ammonium molybdate in an acid solution to form a yellow ammonium silica molybdate complex.[1] This yellow complex is reduced with 1-amino-2-naphthol-4-sulfonic acid reagent to form molybdenum blue. The intensity of color is proportional to the amount of dissolved silica present. The intensity of the color is determined on a spectrophotometer at a wavelength of 815 millimicrons (mμ). Tartaric acid minimizes interference from phosphates. The pH of the sample before addition of reagents must be between 6 and 7. The precision of the method is estimated to be 5%.

Reagents and Chemicals

Deionized distilled water.

Silica standard (sodium metasilicate solution), 200 μg SiO_2/mL: Weigh accurately 0.9510 g of sodium metasilicate, $Na_2SiO_3 \cdot 9H_2O$ (Note 1) and dissolve in 100 to 200 mL of deionized distilled water contained in a 1-liter volumetric flask. Dilute to 1 liter with deionized distilled water, and mix well.

Sulfuric acid - molybdate reagent: Ammonium molybdate, 7.5 g is dissolved in 80 mL of silica-free distilled water, then add 9.0 mL concentrated sulfuric acid and dilute to 100 mL with silica-free distilled water.

Tartaric acid: 10 g dissolved in 100 mL of silica-free distilled water.

1-Amino-2-naphthol-4-sulfonic acid reagent:

Solution "A": Dissolve 9.0 g of sodium bisulfite in 80 mL of silica-free distilled water.

Solution "B": Dissolve 0.7 g of anhydrous sodium sulfite in 10 mL of silica-free water. Add 0.15 g of 1-amino-2-naphthol-4-sulfonic acid and mix until dissolved.

Add Solution B to Solution A and dilute to 100 mL with silica-free distilled water. Store in black taped polyethylene bottle.

Equipment

Transfer pipets

Volumetric flasks, 25 mL

Spectrophotometer

Absorption cells

Procedure

Preparation of Standard Curve

Step 1. Prepare a series of standard solutions containing 10, 20, 30, 40, and 50 μg silica by pipeting aliquots of the silica standard (200 μg SiO_2/mL) into separate 25-mL volumetric flasks.

Step 2. Follow Steps 2 through 5 of *Determination of Sample,* substituting the standard solutions for the sample solution.

Step 3. Plot the absorbancy (as ordinate) versus the concentration in mg silica (as abscissa) on regular graph paper.

Determination of Sample (Make duplicate determinations)

Step 1. Pipet 10 to 50 μg SiO_2 standard solution to a 25-mL volumetric flask. Make volume to ∿20 mL. Run a reagent blank also.

Step 2. Add 0.25 mL of molybdate reagent.

Step 3. Swirl the flask to mix the solution thoroughly. Allow the solution to stand for 5 ±0.25 minutes (Note 2).

Step 4. Add 1.0 mL of tartaric acid solution to the flask and swirl the flask to mix the solution thoroughly.

Step 5. Add immediately 0.25 ml of 1-amino-2-naphthol-4-sulfonic acid solution to the flask and swirl the flask to mix the solution thoroughly. DILUTE TO THE MARK. Allow the solution to stand at least 20 minutes (Note 3) and read with the spectrophotometer as in Step 6.

Step 6. With a spectrophotometer, measure the absorbance of the sample against the blank using a wavelength setting of 815 mμ and 50-mm light-path absorption cells. Record the readings.

Calculations

Using the sample absorbance reading, obtain the μg of dissolved silica from the prepared standard curve.

$$\% \text{ silica} = \frac{\mu g\ SiO_2 \times \text{dilution factor} \times 100}{\text{sample weight (mg)} \times 1000}$$

Notes:

1. This formula, molecular weight 284.2, with 21.14% SiO_2, and assuming 99.5% purity is the basis for the amount to be weighed. If the formula on the bottle is Na_2SiO_3, i.e., anhydrous salt containing 49.23% silica, the quantity to be weighed is 0.4082 g.

2. The time lapse between the addition of sulfuric acid-molybdate reagent and the addition of the tartaric acid reagent and the 1-amino-2-naphthol-4-sulfonic acid reagent is critical and should be timed very closely.

3. The time of development of the molybdenum blue color is complete at 20 minutes and the color is very stable after this period.

REFERENCE

H. H. Willard, L. L. Merritt, Jr., and J. A. Dean. *Instrumental Methods of Analysis*, 3rd ed., D. Van Nostrand Company, New York, N.Y. (1958).

COLORIMETRIC TECHNIQUE FOR THORIUM

Introduction

Thorium is determined only on dissolved sludge samples which SSMS has shown to be less than 1 wt % thorium.

Reagents and Chemicals

Sodium hydroxide, 1M

Nitric acid, 1M

Thorium nitrate solution, 5×10^{-4}M

Thorin reagent, aqueous, 0.1% by weight

Equipment

Spectrophotometer, volumetric flask, and assorted 50-mL micropipets

Absorption cells, 50 mm

Burets, 50 mL

Procedure

Step 1. Place about 10 mL of distilled water in a 50-mL volumetric flask.

Step 2. Pipet a sample containing 10 to 100 micrograms of thorium, but no more than 30 meq (i.e., mL × M) of acid.

Step 3. Determine meq of acid in aliquot taken. Determine the quantity of 1M acid or 1M hydroxide needed to make the total acid or the sample equal to 15 meq.

Step 4. Using a buret, add 5.0 mL of aqueous thorin reagent.

Step 5. Dilute to the calibration mark with distilled water and invert the flask several times to ensure mixing.

Step 6. Prepare a blank by following Steps 1, 3, 4, and 5.

Step 7. Place sample and blank in matched 50-mm absorption cells.

Step 8. Using a spectrophotometer at a wavelength of 545 millimicrons, determine the absorbancy for the standard and the sample solution against the reagent blank set at 0.

Calculations

$$\text{Molarity of thorium} = \frac{A \times B}{C \times D \times 10^4}$$

where:

A = absorbancy of sample solution
B = molarity of standard thorium solution
C = absorbancy of the standard thorium solution
D = sample aliquot used, milliliters

Reference

C. J. Rodden. *Analysis of Essential Nuclear Reactor Materials.* New Brunswick Laboratory, New Brunswick, N.J. (1964). P. 114f

COLORIMETRIC TECHNIQUE FOR URANIUM

Introduction

Uranium was determined by colorimetry for all dissolved sludge samples.

Reagents and Chemicals

Uranium standard solutions

Concentrated HCl

10% stannous chloride solution

8M ammonium thiocyanate solution

Equipment

Volumetric flasks, 25 mL

Spectrophotometer and cells

Procedure

Step 1. Add about 15 mL of distilled water at a 25-mL volumetric flask for the preparation of the reagent blank.

Step 2. Add the recommended aliquot of the standard solution to another 25-mL volumetric flask.

Step 3. Add the appropriate aliquot of sample containing between 0.5 mg and 1.75 mg uranium to a third 25-mL volumetric flask.

Step 4. To each of the three flasks, add the following reagents in the order given:

(a) 5 drops of concentrated hydrochloric acid
(b) 3 mL of 10% stannous chloride solution
(c) 5 mL of 8M ammonium thiocyanate solution

Step 5. Mix thoroughly by swirling the flasks' contents until effervescence has ceased.

Step 6. Dilute to the calibration marks with distilled water. Stopper and invert the flasks until the solution is homogeneous. Remove the stopper after each inversion until gas is no longer released.

Step 7. Match three spectrophotometer cells by comparing optical densities when filled with distilled water. Set the optical density of one of the cells at 0.400 by adjusting the slit width. The other two cells should give optical densities of between 0.395 and 0.405 to be considered as matched.

Step 8. Fill one of the cells with the reagent blank and insert in the No. 1 position of the cell holder. Cap cell. When filling cells with the solution to be read, rinse the cells twice with the solution. Be sure the exteriors of the cells are absolutely clean and dry before reading.

Step 9. Fill another cell with the standard solution and place in the No. 2 position of the cell holder. Cap cell. The standard and blank cells need not be refilled for each sample reading if a series of samples is being run; however, they should not be used after standing for as long as one hour.

Step 10. Fill the third cell with the sample solution and place it in the No. 3 position.

Step 11. Insert the cell holder into the spectrophotometer and zero the instrument using the blank at a wavelength of 380 millimicrons.

Step 12. Measure the optical densities of the standard and sample at 380 millimicrons wavelength.

Step 13. Record the optical densities and aliquots of the standard and sample in a notebook.

Calculations

$$\text{Organic sample:}\quad \text{g/L U} = \frac{A_1 \times V_2 \times C \times F}{A_2}$$

$$\text{Aqueous sample:}\quad \text{g/L U} = \frac{A_1 \times V_2 \times C}{A_2 \times V_1}$$

where:

A_1 = absorbance of sample (optical density units)

A_2 = absorbance of standard (optical density units)

V_1 = sample size, mL

V_2 = aliquot of standard, mL

C = g/L U in standard

F = dilution factor

References

1. C. E. Crouthamel and C. E. Johnson. "Spectrophotometric Determination of Uranium by Thiocyanate Method in Acetone Medium." *Anal. Chem. 24*, 1780 (1952).

2. T. M. Florence. "The Spectrophotometric Determination of Uranium." Paper No. 5 in *Proceedings of a Symposium on the Analytical Chemistry of Uranium and Thorium*, held at Lucas Heights, Sydney, Australia in 1970. Report AAEC/TM 552 (August 1970).

ACID TITRATION FOR ALUMINATE, CARBONATE, AND HYDROXIDE IONS

Introduction

Hydroxide concentration can be determined by the method of pH determinatnion in concentrated salt solutions.[1] This technique gives excellent results over the pH range of 10 to 13. However, in the highly salted solutions above pH 13, the error of ±0.1 pH unit becomes significant in calculating the total free-hydroxide concentration.

To titrate the free base of these higher concentrations, the carbonate is first removed by adding 0.5M barium chloride solution.[2] After centrifugation, the carbonate is determined by dissolving the residue in a known aliquot of standard acid and back titrating with standard base. The free hydroxide is then determined by titrating the hydroxide and aluminate to pH 7; then aluminum is complexed with oxalate, and the solution again titrated to pH 7 to allow calculation of both free hydroxide and the aluminate.

Reagents

- 0.1N HCl, standardized
- 0.1N NaOH, standardized
- 0.5M barium chloride (104 g $BaCl_2$/L)
- 1M potassium oxalate (184 g $K_2C_2O_4 \cdot H_2O$/L)
- Buffer solution, pH 7

Equipment

- Expanded-scale pH meter
- Vortex mixer
- Hot plate
- Centrifuge
- Magnetic stirrer
- Combination glass electrode (such as *Beckman* 39501)
- 15-mL conical centrifuge tubes, with cap
- 1-mL micropipet, such as *Digipet*[a]
- *Teflon*[b] stirring bars, 10 mm × 3 mm

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[a] Registered tradename of Manostat Corp., New York, N.Y.

[b] Registered tradename of E. I. du Pont de Nemours & Co., Wilmington, Del.

10-mL beakers

Micropipets and transfer pipets, as required

Procedure

Step 1. With the glass electrode in pH 7 buffer, adjust the pH meter to read 7.0 on both the standard and expanded scales.

Step 2. Pipet 50 µL (or other appropriate volume) of sample into a centrifuge tube that contains about 2 mL of water.

Step 3. Add ∿1 mL 0.5M $BaCl_2$ solution.

Step 4. Mix on vortex mixer.

Step 5. Centrifuge to separate precipitate.

NOTE: Keep sample in closed centrifuge tube until immediately before the titration (Step 6). This solution is subject to change in composition by absorption of carbon dioxide from the air, with precipitation of barium carbonate; a precipitate in the solution to be titrated is unacceptable.

Step 6. Quantitatively transfer supernate to a 10-mL beaker; rinse tube carefully with about 1 mL of water, taking care not to disturb the precipitate. Add rinse to solution in beaker. (If precipitate is disturbed, centrifuge again before removing supernate.) Replace cap on tube and reserve the precipitate for carbonate determination.

Step 7. Proceed at once to titrate the solution for hydroxyl and aluminate ions as follows:

a. Titrate with 0.1N HCl to pH 7. (Make final adjustment of pH with meter on expanded scale.) Record volume required; call this A.

b. Add 1 mL of 1M potassium oxalate solution. Then add an excess of 0.1M HCl from the refilled buret, so that the pH is permanently at 5 to 6. Record the volume of HCl added to the solution; call this B.

NOTE: The barium ions remaining in solution from the carbonate precipitation step precipitate as barium oxalate which does not interfere in the determination, but does consume oxalate so that the amount of oxalate added must be greater than the barium ion concentration to ensure that sufficient oxalate is available to complex the aluminum.

c. Allow the solution to stir about 1 min. Then titrate with standard 0.1N NaOH to pH 7 (on expanded scale). Record volume of NaOH; call this C.

Step 8. Determine carbonate ion content of precipitate from Step 6 as follows:

a. Add about 1 mL of water and 1000 µL of HCl to the precipitate and agitate to dislodge precipitate. Total volume should be 2 to 4 mL. Mix on vortex mixer.

b. Loosen cap of centrifuge tube and place tube in boiling water for 10 min. Mix again on vortex mixer to expel carbon dioxide gas. (If sulfate is present, all of the precipitate will not dissolve.)

c. Quantitatively transfer solution (with rinse) to a 10-mL beaker and titrate to pH 7 (on expanded scale) with 0.1N NaOH. Record volume required; call this D.

Calculations

V = mL of sample

Titration of Hydroxyl and Aluminate Ions

A = mL of HCl to first end point, Step 7a

B = mL of HCl added in Step 7b

C = mL of NaOH added in Step 7c

Titration of Carbonate Ion

D = mL of NaOH added in Step 8c

$$\text{Molarity of } OH^- + Al(OH)_4^- = \frac{(A)\ (N \text{ of } HCl)}{V}$$

$$\text{Molarity of } Al(OH)_4^- = \frac{(B)\ (N \text{ of } HCl) - (C)\ (N \text{ of } NaOH)}{3\,V}$$

$$\text{Molarity of } OH^- = [(1) - (2)]$$

$$\text{Molarity of } CO_3^{2-} = \frac{(1.000)\ (N \text{ of } HCl) - (D)\ (N \text{ of } NaOH)}{2\,V}$$

References

1. E. W. Baumann. *Volumetric Determination of Hydroxide, Aluminate, and Carbonate in Alkaline Solutions of Nuclear Waste*. USERDA Report DP-1386, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S.C. (1975).

2. Takoa Yatsuyangi, Masaru Yamada, and Kazuo Aomura. "Reaction Equilibrium of Aluminate with Oxalate and Its Application to Potentiometric Titration of Aluminate." *Hokkaido Daigaku Kogakubu Kenkyu Hokoku,* 1970 (55), 73-80 (Japan); CA 73, 51900h (1970).

ACID TITRATION FOR ALUMINUM IN DISSOLVED SLUDGE

Introduction

Aluminum is a major constituent in Savannah River Plant waste tank sludge. Analyses by normal titration methods, e.g., EDTA, are hampered by interferences, e.g., iron and calcium. Aluminum can be separated from most interferences by precipitation with NaOH. Care must be taken to assure that sufficient NaOH is added to redissolve all of the aluminum. This is best accomplished by adding the acid solution to an equal aliquot of NaOH solution, where the NaOH concentration is twice the acid concentration. If the separation is made in the reverse manner, low results for aluminum are obtained. Once the separation is made, the aluminum can be determined either by titration as if the solution were a supernate solution, or the solution may be acidified and titrated by EDTA. For consistency, the former method is normally used. Alternately, aluminum can be determined by atomic absorption.

Reagents

6M NaOH

0.1N HCl, standardized

0.1N NaOH, standardized

0.5M barium chloride (104 g $BaCl_2$/L)

1M potassium oxalate (184 g $K_2C_2O_4 \cdot H_2O$/L)

Buffer solution, pH 7

Equipment

Expanded-scale pH meter

Vortex mixer

Hot plate

Centrifuge

Magnetic stirrer

Combination glass electrode, such as *Beckman* 39501

15-mL conical centrifuge tubes, with cap

Micropipet, such as *Digipet*,[a] 1 mL

Teflon[b] stirring bars, 10 mm × 3 mm

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[a] Registered tradename of Manostat Corp., New York, N.Y.

[b] Registered tradename of E. I. du Pont de Nemours & Co., Wilmington, Del.

10-ml beakers

Micropipets and transfer pipets, as required

Procedure

Step 1. Add 5.0 mL of 6 to 8M NaOH to a centrifuge cone.

Step 2. Pipet 5.0 mL of sludge stock solution (3M HCl solution) to the NaOH in the centrifuge cone.

Step 3. Mix well on a vortex mixer.

Step 4. Centrifuge.

Step 5. Pipet aliquots of sample for aluminum analysis.

Step 6. Complete the analysis for aluminum by the titration procedure mentioned above.

Calculations

Perform calculations as given in the titration procedure mentioned above.

EDTA TITRATION FOR ALUMINUM

Introduction

Aluminum can be determined by EDTA titration as a cross-check on other methods. The dissolved aluminum, in 3M HCl, is separated from interfering ions by adding the sample to an equal volume of 8M NaOH.

The aluminum concentration is determined by complexing with an excess of a standard EDTA solution (Note 1), then back-extracting the excess EDTA with a standard lanthanum solution.

Reagents and Chemicals

All solutions listed below should be prepared in deionized water.

Nitric acid, 0.1M: Measure 0.63 mL (Mohr pipet) of concentrated nitric acid into a 100-mL graduate, and dilute to 100 mL with deionized water.

Sodium hydroxide, 1.0M: Weigh 4 g of sodium hydroxide pellets and dissolve in 25 to 50 mL of water. Dilute this solution to 100 mL with water.

Sodium hydroxide, 0.1M: Measure 10 mL of the 1.0M sodium hydroxide; dilute to 100 mL.

Arsenazo solution, 0.25%: Weigh 0.250 to 0.251 g of arsenazo solid; dissolve in 100 mL of deionized water.

Methyl red, 0.1% in ethyl alcohol: Weigh 0.10 g of methyl red solid; dissolve in 100 mL of 95% ethyl alcohol.

EDTA solution, 0.01M: Weigh accurately 2.95 to 3.00 g of EDTA powder (Note 2). Transfer to a 600- to 800-mL beaker; rinse weighing vessel with deionized water. Slurry the powder in 200 to 400 mL of deionized water (Note 3). Add 1M NaOH solution carefully to neutralize (pH ∿7.0) to the tetrasodium salt stage. All powder should be dissolved at this stage. Transfer solution to a 1000-mL volumetric flask and dilute to volume with deionized water. Mix well (Note 4).

Lanthanum standard solution, ∿0.02M: Weigh accurately 0.8660 to 0.8665 g of lanthanum nitrate, $La(NO_3)_3{\cdot}6H_2O$. Dissolve in 40 to 50 mL of deionized water and dilute to 100 mL with deionized water in a 100-mL volumetric flask. Mix well (Note 4).

Equipment

- Microburet
- Beakers, 50 mL, 600 mL, 800 mL
- Micropipets
- Dropping pipets
- Magnetic stirrer and stirring bars
- Volumetric flasks, 1000 mL
- Graduates, 100 mL

Procedure

Step 1. Measure about 15 mL of deionized water into a 50-mL beaker set on a magnetic stirrer; add a stirring bar.

Step 2. Pipet a quantity of sample solution containing 0.002 to 0.006 millimole of aluminum into the beaker.

Step 3. Add 1 mL (micropipet) of standard EDTA solution.

Step 4. Add 2 drops of methyl red indicator solution.

Step 5. Adjust the pH by careful addition of 0.1M NaOH until the solution is just yellow. If the end point is overstepped, readjust the pH with 0.1M nitric acid.

Step 6. Add one drop of pyridine.

Step 7. Add one drop of arsenazo solution.[1]

Step 8. Using a microburet, titrate the solution with 0.02M standard lanthanum solution until the color changes from orange to violet. Record volume of the lanthanum solution required (mL_{La}).

Calculations

$$M_{Al} = (M_{EDTA} \times mL_{EDTA} - M_{La} \times mL_{La})\ (\text{Dilution factor})$$

Notes:

1. EDTA is (ethylenedinitrilo) tetraacetic acid $(CO_2HCH_2)_2N\text{-}C_2H_4\text{-}N(CH_2CO_2H)_2$, molecular weight 292.25. The material may also be called ethylenediaminetetraacetic acid.

2. EDTA as a dry solid is a white free-flowing powder, 99.9 to 100% pure; hence, a given molarity may be made by accurate weighing and dissolving the required amount. EDTA is only sparingly soluble in water; neutralization with NaOH forms the very soluble tetrasodium salt.

3. Deionized water should be used in preparation of all reagents, samples, and standards for EDTA titrations.

4. The EDTA in excess of that required to react with the aluminum is back-titrated with lanthanum solution. For this reason, although the reagents are essentially pure, a comparison of the EDTA solution and the lanthanum solution should be made by actual titration. Other lanthanum components, e.g., lanthanum chloride or lanthanum oxide, may be used as standards for preparing lanthanum standard solutions.

Reference

1. J. S. Fritz, R. T. Oliver, and D. J. Pietryzk. "Chelometric Titrations Using an Azoarsonic Indicator." *Anal. Chem. 30*, 1111 (1958).

DIRECT TURBIDITY METHOD FOR DETERMINING SULFATE ION CONCENTRATIONS IN LEACH SOLUTIONS AND SUPERNATES

Introduction

Sulfate is determined by the turbidity method on supernate and interstitial liquid samples without prior treatment. Sulfate in dissolved samples may also be determined by the direct method to determine the upper limit of sulfate; however, these numbers may be high by factors of 10 to 100. After pretreatment of the dissolved samples to remove interfering ions (mainly ferric ion), the turbidity method gives a more reasonable sulfate analysis.

Reagents and Chemicals

Sulfate reagent: the chemicals in this reagent must be added in the following order:

(a) Dissolve 100 g $BaCl_2$ in ∿400 mL of distilled water.

(b) Add 20 g NaCl after the $BaCl_2$ has completely dissolved.

(c) After the $BaCl_2$ and NaCl have completely dissolved, add 280 μL of ethanol.

(d) Add 4 mL of glycerol.

(e) Dilute to 1000 mL with distilled water.

Sulfate standard

Equipment

Pipets

Volumetric flasks, 10 mL

Colorimeter

Procedure

Step 1. Add ∿5 mL of sulfate reagent into a 10-mL volumetric flask.

Step 2. Pipet sample into flask.

Step 3. Dilute to mark with sulfate reagent and invert gently.

Step 4. Set stand for 15 minutes.

Step 5. Read sample at 380 nm.

Step 6. Prepare standard reference samples as above.

Calculations

Draw a calibration curve using the standard reference samples. Read the sulfate concentrations of the samples directly from the calibration curve.

INDIRECT TURBIDITY METHOD FOR DETERMINING SULFATE ION CONCENTRATIONS IN DISSOLVED SLUDGE

Introduction

The Fe, Mn, Ni, alkaline earths, lanthanides, and actinides are precipitated by the addition of a sample (in 3M HCl) to twice the aliquot volume of 6M NaOH. If added in this order, the sulfate ions remain in solution. However, if added in the reverse order, the sulfate ions are carried by the precipitate. This indirect method reduces interferences so that the turbidity method can be used; interferences are not, however, eliminated. The method does allow the estimation of sulfate ion concentrations to within a factor of 2 to 10.

Reagents and Chemicals

6M NaOH

Equipment

Centrifuge cones

Slurry pipets

Assorted pipets

Procedure

Step 1. Pipet 10.0 mL of 6M NaOH into a centrifuge cone.

Step 2. Slowly pipet 5.0 mL of sample into the same centrifuge cone.

Step 3. Centrifuge sample.

Step 4. Transfer solution out of the cone with a slurry pipet.

Step 5. Analyze sample aliquot by the turbidity method.

Calculations

See the direct turbidity method above.

Note: Remember the above dilution factor in the calculations.

DETERMINATION OF CHARCOAL IN INSOLUBLE RESIDUE

Introduction

Charcoal in the sample of insoluble residue is determined by bringing the sample to constant weight over a Meker burner and assuming the weight loss to be carbon.

Reagents and Chemicals

None.

Equipment

Meker burner

Platinum crucible

Balance

Procedure

Step 1. Bring a platinum crucible to constant weight over a Meker burner.

Step 2. Weigh accurately a sample of about 0.5 to 1.0 g, more or less.

Step 3. Bring sample to constant weight over a Meker burner.

Calculations

$$\%\ C = \frac{A - B}{A} \times 100$$

where:

A = weight sample

B = weight residue

DETERMINATION OF SILICA IN INSOLUBLE RESIDUE

Introduction

The residue from the charcoal determination is used for the determination of silica.

Reagents and Chemicals

HF

Equipment

Meker burner

Platinum crucible

Balance

Procedure

Step 1. Add a few drops HF to the residue from the charcoal determination.

Step 2. Heat over a Meker burner.

Step 3. Repeat Steps 1 and 2 until sample comes to constant weight.

Calculations

$$\% \ SiO_2 = \frac{B - C}{A} \times 100$$

where:

A = weight original sample

B = weight carbon determination residue

C = weight HF treatment residue

DETERMINATION OF ALUMINA IN INSOLUBLE RESIDUE

Introduction

A weighed sample of insoluble residue is fused with potassium pyrosulfate and then dissolved in nitric acid. After dilution to a known volume, the sample is analyzed by atomic absorption analysis.

Reagents and Chemicals

Potassium pyrosulfate

Nitric acid, 1M

Equipment

Meker burner

Platinum crucible

Balance

Procedure

Step 1. Accurately weigh a sample of insoluble residue into a platinum crucible.

Step 2. Add about 5 times the sample weight of potassium pyrosulfate.

Step 3. Fuse the sample over a Meker burner.

Step 4. Cool and dissolve the cake in 1M nitric acid.

Step 5. Submit the sample to the atomic absorption lab for analysis.

Calculations

$$\%\ Al_2O_3 = \frac{\text{mg Al/L} \times \text{volume, L}}{\text{weight of sample, mg}} \times \frac{101.96}{2 \times 26.9815} \times 100$$

$$= \frac{\text{mg Al/L} \times \text{volume, L}}{\text{weight of sample, mg}} \times 188.94$$

REMOVAL OF RADIOACTIVE CESIUM

Introduction

Supernate samples and interstitial liquid samples are usually so intense in ^{137}Cs gamma radiation that counting of the other isotopes is impractical. Therefore, the ^{137}Cs is removed by adsorption on a zeolite column. The remaining gamma-emitting isotopes can then be counted.

Reagents and Chemicals

Zeolite

Distilled water

NaOH

Equipment

Ion exchange columns

Pipets

Volumetric flasks

Procedure

Step 1. Load a short ion exchange column with about 5 mL of zeolite resin.

Step 2. Wash the zeolite with water.

Step 3. Load 1 mL of sample into the column. (If sample is less than pH 8, make the sample basic first.)

Step 4. Catch eluate in volumetric flask. Wash column with water. Combine eluate and washings.

Step 5. Dilute to volume.

Step 6. Prepare gamma tube by normal procedure for gamma-PHA.

REMOVAL OF INTERFERING IONS VIA AN ALUMINA-FILLED COLUMN

Introduction

Due to the variable high bias of the base conversion method for removing interfering ions, the cleanup procedure for the samples was changed to an alumina-filled column method. In general, the sample aliquot is diluted to about 1M H^+ with distilled water before loading onto an alumina column. The interfering cations pass through the column while sulfate is retained. After washing the column, sulfate ions are removed with an ammonia solution.[1] This solution is then evaporated to near dryness. The residue is dissolved and analyzed by the turbidity method.

Reagents and Chemicals

Distilled water

0.1M and 1M ammonium hydroxide solutions

Activated alumina, 80 to 200 mesh, chromatographic grade

Equipment

Alumina column

Hot plate

Volumetric flasks, 10 mL

Beakers

Pipets

Slurry pipes

Procedure

Step 1. Add some chromatographic grade alumina (80 to 200 mesh) to a beaker, wash with water, and allow precipitate to settle.

Step 2. Decant the supernatant liquid and repeat the washing process until the very fine particles have been removed, as evidenced by clear wash water.

Step 3. Transfer the alumina to a column.

Step 4. Wash with 50 mL of 1M ammonium hydroxide solution, several 5-mL portions of 0.1M ammonium hydroxide solution, and finally with approximately 50 mL of water.

Step 5. Wash with 10 mL of HCl of the same strength as the sulfate sample.

Step 6. Dilute a sample aliquot (3M HCl) with an equal volume of distilled water.

Step 7. Pass an aliquot of the diluted sample through the alumina column at the rate of approximately 120 drops per minute.

Step 8. Wash the column with 10 mL of 4 vol % HCl.

Step 9. Wash the column with 25 mL of distilled water added in several portions.

Step 10. Elute the sulfate from the column by adding successively 5 mL of 1M ammonia, 20 mL of 0.1M ammonia, 20 mL of 0.1M ammonia in 5-mL portions, and about 25 mL of water.

Step 11. Pass the sulfate-containing effluent through a 1-inch by 3-inch-column filled with *Dowex* 50-X8, 20- to 50-mesh, cation exchange resin (acid form).

Step 12. Wash the cation column with about 40 mL of distilled water.

Step 13. Evaporate the sample to about 5 mL. Quantitatively transfer to a 10-mL volumetric flask and dilute to the mark.

Step 14. Determine the sulfate by the turbidity method (above).

Calculations

See direct turbidity method above.

NOTE: Do not allow the column to run dry.

Reference

1. J. S. Fritz, S. S. Yamamura, and M. J. Richards. "Titration of Sulfate Following Separation with Alumina." *Anal. Chem.* *29*, 158 (1957).

APPENDIX C: ION CHROMATOGRAPHIC ANALYSIS OF WASTE SOLUTIONS

INTRODUCTION

While this report was in press, a *Dionex*® Model 14 ion chromatograph was purchased. Ion chromatograph techniques were then developed to determine nitrate, nitrite, sulfate, phosphate, fluoride, chloride, sodium, potassium, and ammonium ion concentrations. Tests with synthetic waste supernate showed that alkali cations, halides, and oxyanions at the ppm concentration could be separated and detected. Typical multi-ion solutions could be analyzed in 30 minutes. For completeness, a discussion of the ion chromatograph technique is given below. This technique has replaced several of the techniques mentioned in the body of this report and discussed in Appendix B.

TECHNIQUE OF ION CHROMATOGRAPHY

Ion chromatography combines the advantages of ion-exchange separation and conductivity detection. Although ion exchange resins provide excellent separation of ions, analysis of the eluted species is often hindered by the presence of the background electrolyte used for elution. By using a novel combination of resins, Small, Stevens, and Bauman[1] were able to separate the ions in a sample, suppress the background, and then use a conductivity cell to detect and measure either anions or cations from the sample. Two ion-exchange columns were used in series, the first for conventional ion-exchange separation and the second for suppression of the eluent background conductivity.

Table C-1 summarizes the differences between ion chromatography and classical ion-exchange chromatography. The ion chromatograph permits rapid analysis of multi-ion mixtures with a high degree of sensitivity.

The *Dionex*® ion chromatograph uses a second ion-exchange column to suppress the conductivity of the eluent while leaving the sample ions unaffected. Because the suppressor column

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® Trademark of Dionex Corporation, Sunnyvale, California.

[1] H. Small, T. S. Stevens, and W. C. Bauman. "Novel Ion Exchange Chromatographic Method Using Conductometric Detection." Anal. Chem. 47, 1801 (1975).

TABLE C-1

Comparative Features of Ion-Exchange Analysis and Ion Chromatography

Ion-Exchange Analysis	*Ion Chromatography*
Strong eluents (0.1 to 10 molar)	Weaker eluents (1 to 10 millimolar)
Single ion analysis	Multiple ion analysis
High-capacity resin	Low-capacity separator resin (pellicular)
No suppressor column	Suppressor column
Slow and labor-intensive	Fast and easy, equipment simple
Secondary quantitation by classical methods	Online conductimetric detection
Detection limited by secondary analytical method	Detection limited by species conductivity
Capable of transition-metal analysis	Presently very limited capability for transition-metal analysis

accumulates ions removed from the eluent, it has to be regenerated periodically to delay breakthrough. This regeneration requirement limits eluent concentrations and the type and design of the ion-exchange columns.

Ion Chromatography System

The *Dionex*® Model 14 ion chromatograph incorporates the complete system needed for ion chromatography. The system includes two pumps, valves, two sample injection loops, and a conductivity cell (Figure C-1). Although there are two complete sets of columns, the Model 14 has only one conductivity cell and one regeneration pump. Thus, one set of columns can be used for analysis while the other set of columns can be regenerated.

Pneumatic valves control sample injection and eluent flow through the separator and suppressor columns. Sample volumes can range up to 1000 mm^3, although 100 mm^3 is typical. The Model 14 can determine cations or anions, can regenerate one set of columns while the other is being used for ion analysis, and can switch to different eluents.

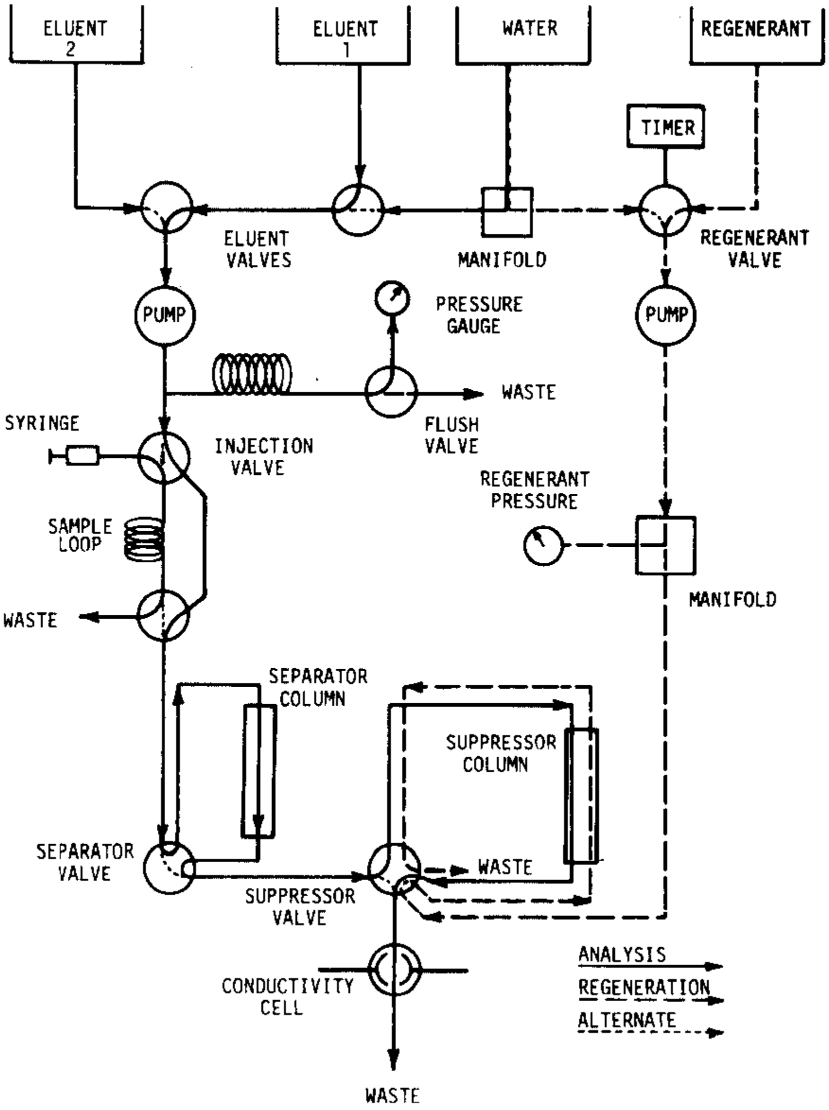

FIGURE C-1. *Dionex*® Ion Chromatography System

ANALYSES

Anion Analysis

Sodium hydroxide solution can be used as the eluent in anion analysis. After passing through the separator column, the sample anions will appear at different times in an NaOH background. The solution then passes through the suppressor column containing a strong acid cation-exchange resin where the following reactions occur:

$$(\text{Resin-H}^+) + \text{Na}^+ + \text{OH}^- \leftrightarrows (\text{Resin-Na}^+) + \text{H}_2\text{O}$$

$$(\text{Resin-H}^+) + \text{Na}^+ + \text{X}^- \leftrightarrows (\text{Resin-Na}^+) + \text{HX}$$

Thus, NaOH is removed and appears as water, while sample anions (X^-) are eluted from this second column in the acidic form in a water background of low conductivity. The solution then passes through a conductivity cell where the anions are detected. The only requirement is that the acid form of the anion (HX) be sufficiently ionized ($pK_a \leqslant 7$) for detection with the conductivity cell.

Other eluents such as a mixture of sodium carbonate and sodium bicarbonate can be used for anion analyses because they are converted to carbonic acid, which has a low conductivity. The sodium carbonate/sodium bicarbonate eluent is usually used for anion analysis because it provides better control of pH.

Cation Analysis

Nitric acid solution is used as the eluent for cation analysis. After being separated by the separator column, the cations appear in a background of nitric acid. The solution then passes through the suppressor column containing a strong base anion-exchange resin where the following reactions occur:

$$(\text{Resin-OH}^-) + \text{H}^+ + \text{NO}_3^- \rightleftarrows (\text{Resin-NO}_3^-) + \text{H}_2\text{O}$$

$$(\text{Resin-OH}^-) + \text{M}^+ + \text{NO}_3^- \rightleftarrows (\text{Resin-NO}_3^-) + \text{MOH}$$

Sample cations (M^+) are now present as metal hydroxides (MOH) and the nitric acid has been converted to water. Cations can be detected by the conductivity cell if $pK_b \leqslant 7$ for the metal hydroxides.

PERFORMANCE TESTS WITH STANDARD SOLUTIONS

Performance of the ion chromatograph was tested with a *Dionex®* standard anion solution (3 ppm F^-, 4 ppm Cl^-, 10 ppm NO_2^-, 50 ppm PO_4^{3-}, 10 ppm Br^-, 30 ppm NO_3^-, and 50 ppm SO_4^{2-}) and a *Dionex®* standard cation solution (6.4 ppm Na^+, 4.1 ppm NH_4^+, and 12.6 ppm K^+). A 3-mm x 500-mm separator column and 0.003M $NaHCO_3$/0.0024M Na_2CO_3 eluent were chosen for anion analysis. A 6-mm x 250-mm separator column and 0.010M HNO_3 eluent were chosen for cation analysis. Column efficiency, instrument performance, and operator technique were checked by measuring elution time, chromatographic resolution, and number of theoretical plates.

Elution Time

Ions in samples are identified by comparing elution times of unknown peaks with elution times for ions in *Dionex®* standard solutions (Table C-2). Elution times are also a measure of the selectivity of the ion-exchange column for each ion compared to ions in the standard solutions; the longer the elution time, the stronger the affinity for the sample ion.

Resolution

Chromatographic resolution is defined by the time (distance on chart) between the centers of two peaks divided by the average base width of those two peaks. Table C-2 lists the resolution between a particular ion and the ion following it in the table for the *Dionex®* standard solutions. At these concentrations, the ions are generally well resolved, although some overlap between bromine ion and nitrate ion is indicated by the small resolution.

Column Efficiency

The number of theoretical plates, N, a measure of column efficiency, is given by

$$N = 16(V/W)^2$$

where V is the elution time and W is the base width of the peak. Table C-2 lists N for each ion in the *Dionex®* standards.

Calibration

Calibration curves were constructed at both 30 μmho and 10 μmho full-scale by measuring the conductivities of five solutions containing Cl^-, F^-, PO_4^{3-}, NO_2^-, SO_4^{2-}, and NO_3^- at

TABLE C-2

Performance of Ion Chromatograph
with Standard Solutions

Anions[a]	*Elution Time, min*	*Resolution*	*Number of Theoretical Plates*
F^-	2.1	3.25	440
Cl^-	3.4	1.60	1160
NO_2^-	4.2	2.56	785
PO_4^{3-}	6.3	1.75	390
Br^-	8.4	0.81	680
NO_3^-	9.7	2.0	425
SO_4^{2-}	14.4	-	380
Cations[b]			
Na^+	7.8	2.23	970
NH_4^+	10.7	1.41	800
K^+	13.1	-	850

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[a] *Dionex®* standard anion solution; 0.003M $NaHCO_3$/0.0024M Na_2CO_3 eluent.

[b] *Dionex®* standard cation solution; 0.010M HNO_3 eluent.

concentrations covering 10 to 80% of full scale. Similar calibration curves were constructed for Na^+, K^+, and NH_4^+.

From these calibration curves, the minimum detection limit (signal-to-noise ratio about 2) at the most sensitive conductivity setting was derived for each ion, together with the concentration range within which the ion could be routinely determined. Table C-3 lists these detection limits and concentration ranges for each ion. Detection limits are about 0.01 ppm for halides and about 0.1 ppm for other ions. Detection limits can be lowered by factors of 10 to 100 for special samples by using another column to concentrate the ions before analysis by the ion chromatograph.

Accuracy and Precision

Reproducibility of the ion chromatograph was determined by 10 replicate measurements of a solution containing 10 ppm NO_2^-, 10 ppm NO_3^-, and 10 ppm SO_4^{2-}, and of a solution containing 1 ppm Cl^-, 1 ppm F^-, and 10 ppm PO_4^{3-}. Table C-4 compares actual and measured concentrations (accuracy) and lists the standard deviation of replicate measurements (precision) for each ion. Measured concentrations are within 2% (for sulfate ion) to 10% (for chloride ion) of the actual concentrations. Relative standard deviations range from 2% for phosphate ion to 9% for nitrite ion concentrations.

TESTS WITH SYNTHETIC WASTES

Supernate and Interstitial Solution

Synthetic waste supernate and interstitial solutions were analyzed for nitrite, nitrate, sulfate, and sodium ions by ion chromatography. Since the concentrations of these ions were in the molar range, solutions were diluted 1:2000 for anion analysis and 1:10,000 for Na^+ analysis. Each diluted solution was analyzed five times. Table C-5 shows that measured concentrations agreed reasonably well with concentrations as prepared. However, the analytical precision was only ±20% to ±40% for nitrite ion.

Sludge

Dried synthetic sludge was dissolved in 1M HCl and diluted to bring the concentrations of nitrate and sulfate ions into the proper range. The solution was analyzed ten times. Table C-6 shows that measured concentrations of nitrate, sulfate, and sodium ions agreed reasonably well with the concentrations as

TABLE C-3

Analytical Capability of Ion Chromatograph

Ion	*Concentration Range for Routine Determination, ppm*	*Minimum Detection Limit, ppm*
F^-	0.06 to 7	0.009
Cl^-	0.20 to 20	0.025
NO_2^-	0.5 to 60	0.05
PO_4^{3-}	1.0 to 120	0.1
NO_3^-	1.3 to 150	0.1
SO_4^2	1.1 to 130	0.1
Na^+	0.5 to 20	0.05
NH_4^+	2 to 150	0.2
K^+	3 to 120	0.1

TABLE C-4

Accuracy and Precision of Ion Chromatographic Analyses of Standard Solutions

	Accuracy			*Precision*	
Anion	*Known Concentration, ppm*	*Average Measured Concentration, ppm*	*% Diff.*	*Standard Deviation, ppm*	*Relative Std. Dev., %*
F^-	1	0.95	5	0.02	2
Cl^-	1	1.10	10	0.04	4
NO_2^-	10	9.03	9.7	0.87	8.7
NO_3^-	10	10.26	2.6	0.35	3.5
SO_4^{2-}	10	9.8	2	0.43	4.3
PO_4^{3-}	10	9.5	5	0.19	1.9

TABLE C-5

Ion Chromatographic Analyses of Synthetic Waste Supernate and Interstitial Solution

Supernate	*Known Concentration, M*[a]	*Measured Concentration, M*[b]
NO_2^-	1.1	0.96 ±0.20
NO_3^-	2.2	1.94 ±0.04
SO_4^{2-}	0.30	0.28 +0.005
PO_4^{3-}	5.25	5.26 ±0.11
Interstitial Solution		
NO_2^-	1.0	1.15 ±0.39
NO_3^-	2.0	1.82 ±0.02
SO_4^{2-}	0.30	0.24 ±0.005
PO_4^{3-}	4.2	4.16 ±0.09

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[a] As prepared.

[b] 95% confidence limits.

TABLE C-6

Ion Chromatographic Analyses of Dissolved Synthetic Waste Sludge

Ion	*Known Concentration, wt %* [a]	*Measured Concentration, wt %*
NO_2^-	11.2	5.2[b]
NO_3^-	29.7	33.4 ±0.3[c]
SO_4^{2-}	7.0	5.9 ±0.2[c]
Na^+	23.3	20.9 +0.55[c]

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[a] As prepared.

[b] Only one measurement.

[c] 95% confidence limits.

prepared. However, the strong chloride ion peak from the HCl solution was broad enough to obscure the nitrite ion peak. Attempts to resolve these peaks by using a second separator column and a weaker eluent (0.003M $NaHCO_3$, 0.0003M Na_2CO_3) were not successful. Although the weaker eluent apparently resolved the two peaks, sulfate ion was not detected after 60 minutes.

To determine nitrite ion concentration, another portion of dried synthetic sludge was dissolved in 0.5M H_2SO_4 and the solution was diluted. But a single analysis indicated nitrite ion concentration only half the as-prepared concentration. The poor accuracy of this determination, and the poor precision of replicate nitrite ion determinations in supernate and centrate (above), is due to interaction of weak nitrous acid with the suppressor resin. This interaction causes changes in reaction time and peak height as the sites on the suppressor resin become occupied.