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Laser Raman Spectrometric Determination of Oxy-Anions In Nuclear Waste Materials

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LASER RAMAN SPECTROMETRIC DETERMINATION OF OXY-ANIONS IN NUCLEAR WASTE MATERIALS

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ABSTRACT

Oxy-anions in complex nuclear process-waste materials are being determined by laser Raman spectrometry (LRS). The double internal-standard technique developed by Marston is applied to the simultaneous determination of up to six anions in alkaline solutions. The method of Marston has been extended to solutions prepared from the solids formed in nuclear waste storage tanks. As many as six anions, aluminate, chromate, nitrate, nitrite, phosphate, and sulfate, are simultaneously determined in about one hour. Carbonate may also be determined, but in the presence of the prevalent nitrate, a chemical separation is required. Individual methods have been relegated to a secondary status due to the many advantages of LRS. Advantages such as small sample size, speed of analysis, accuracy, and specificity will be discussed. The typical precision obtained for analytes in high concentration is around five percent relative standard deviation.

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INTRODUCTION

The chemical processing of irradiated nuclear fuels has resulted in large quantities of nuclear wastes which occur in three general types: concentrated aqueous liquor, water soluble salt cake, and sludge of insoluble salts and hydroxides. The major species, other than water, are sodium salts of oxy-anions and the hydroxides of aluminum and iron. The analysis of these nuclear waste materials presents a difficult task due to the concentrations and complexity of the samples. Table I shows a likely composition of waste samples. Compositions may vary widely and many other species may be present in trace amounts. The methods used in the past have largely been trace methods for speed, dilution of the matrix, and freedom from interference. Examples are specific ion electrode and spectrophotometric methods.

Knowledge of anion concentrations is important to monitoring the integrity of the nuclear waste storage, to research in developing nuclear waste solidification methods, and to current processes for processing waste liquors to salt cake.

Irish and Chen (1) have described the use of laser Raman spectroscopy (LRS) for determining oxy-anions. A. L. Marston (2) of the Energy Research and Development Administration's Savannah River nuclear plant has applied laser Raman spectroscopy to the determination of oxy-anions in the Savannah River Plant's waste supernate liquors.

The work described here includes the application of Marston's method to Hanford waste liquors, the use of LRS in analyzing salt cake, sludge, and the LRS determination of carbonate.

EXPERIMENTAL

Spectra are obtained on a Spex Industries Ramalog-5, which has 1800 groove/mm holographic gratings, photon counting system, and a spectral band pass of 3 cm^{-1}. The 5145 Å line of a Coherent Radiation CR-5 argon laser is used. Special 'capillary pipets' are used (Figure 1) to inject samples into melting point capillaries. The capillaries are sealed for control of radioactivity by folding masking tape over the end. The capillary pipets are used with a syringe as in Figure 1.

Waste Liquors. Waste liquors are usually filtered through Millipore BDWP-1300 0.6 μm filters. Marston's method is applied directly to solutions with the following changes:

0.1 ml of 1<u>M</u> $NaClO_4$ and 0.1 ml of sample are diluted into 0.5-1 ml of 1<u>M</u> NaOH in a 2-dram vial, except for samples of low nitrate concentration, when the 0.1 ml of $NaClO_4$ is added directly to 1.00 ml of sample. Micro pipets are rinsed in the mixed aliquots.

<u>Salt Cakes</u>: The salt samples are dissolved in water at 200-300 grams per liter (g/ℓ) concentration and analyzed as a waste liquor.

<u>Sludges</u>. Samples are dissolved in 6<u>M</u> HCl at 1 g/3 ml, excess 13<u>M</u> NaOH (1 ml) added, and the anions determined on the centrifugate.

<u>Calibration</u>. Standard solutions were prepared by dissolving high purity Al wire in several molar NaOH, adding weights of dried $NaNO_2$ and $NaNO_3$ (as the internal standard). The solution volumes were determined by density and the total weight. Calibrations for the other anions were accomplished by Marston's calibration technique. Care had to be exercised during the PO_4^{3-} calibration to stay within the solubility of Na_3PO_4. Spectra had to be taken promptly after mixing solution aliquots of KH_2PO_4, NaOH, and $NaNO_3$ to avoid precipitation of $Na_3PO_4 \cdot 12H_2O$.

Carbonate Determination. The carbonate-nitrate separation is accomplished with the still shown in Figure 2. The still contains 10 percent H_3PO_4; the separatory funnel, carbonate-free 1M NaOH. After purging the still with nitrogen, NaOH solution is admitted to the trap to a depth of 9-10 cm. Nitrogen is then adjusted to a flow which is just short of pushing the NaOH catch solution into the bulb at the top of the trap. Sample aliquots are introduced through the septum with a 2.5 ml Hamilton micro-syringe. Quantitative distillation is obtained within 10 minutes. The catch solution is then drained into a 2-dram vial, 0.25 ml of 1M $NaClO_4$ added; and the ratio, $\frac{I_{CO_3^=}(1070\ cm^{-1})}{I_{ClO_4^-}(935\ cm^{-1})}$, measured with the Raman Spectrometer. Multiple sample aliquots may be added until the still is either full or the acid is exhausted. Calibration may be performed with distilled and/or undistilled standard aliquots.

Individual Methods. Data on individual methods was largely produced by technicians in a rotating shift operation. Individual methods are atomic absorption spectrometry (AA), gravimetric (grav) by absorption of evolved CO_2, non-dispensive infrared absorption (NDIR) of evolved CO_2, with an Oceanography International Corporation carbon analyzer, and spectrophotometric (spec.) measurement of extracted molybdophosphoric acid (3) complex.

RESULTS AND DISCUSSION

The method described by Marston takes advantage of the high relative sensitivity and high concentration of nitrate in nuclear waste liquor to use it as a secondary internal standard for calculating the concentration of other oxy-anions. Nitrate is measured in relation to the primary internal standard, perchlorate, in a dilution. By this double-internal standard technique, the concentration of other anions are determined on the neat sample. Inspection of Table I indicates that this technique may be directly applied to dissolutions of salt cake. Solutions of sludges may not contain significant nitrate. In such cases, standard nitrate is added as a primary internal standard.

Spectral Characteristics. Table II contains the relative molar intensities of all the anions of interest along with the comparable values of Marston. Unexpectedly, the intensity of the nitrite lines is greater in waste liquor type matrices than in a water matrix such as Marston used to calibrate. The observation of this phenomenom has been well substantiated by comparing various solutions containing molar concentrations of $NaAl(OH)_4$, $NaOH$, $NaNO_3$, and $NaNO_2$ with solutions containing molar concentrations of $NaNO_3$, $NaNO_2$, and low molar $NaOH$.

The relative molar intensity of chromate has been determined to be about 5.7, with 5145Å excitation. The intensity of 10, obtained by Marston, is due to preresonance because the 4880Å line used by Marston is closer to the $CrO_4^=$ absorption than is the 5145Å line. Due to the unusual shape of the Raman band of the A_1 stretching mode of chromate, the peak intensity is measured from the maximum intensity to the inflection point at the top of the shoulder (Figure 3). It is measured in this way for quantitative determinations because the shoulder is not detectable at concentrations less than 0.001<u>M</u>. In addition, the background is difficult to determine accurately, since the peak is so broad. A linear calibration plot from 0.0003-0.8<u>M</u> $CrO_4^=$ was obtained using this method.

The intense broad chromate peak is a spectral interferant for both nitrite and phosphate, as has occurred in Figure 3. There is no other analytical line for phosphate, but for nitrite the 1330 cm^{-1} line may be used. However, nitrate with its weak band at about 1410 cm^{-1} interferes. This interference is easily subtracted away by means of a correction factor. Correction factors are used and determined by the technique of MacNevin, <u>et al</u>. (4). This nitrate correction to the 1330 cm^{-1} line is valid for nitrate/nitrite concentration ratios less than 100.

Marston described the sulfate 613 cm^{-1} line as a spectral interference for aluminate. A correction factor is applied to remove the interference when the 985 cm^{-1} sulfate line is greater than twice the aluminate intensity at 623 cm^{-1}.

The only other spectral interference is between $CO_3^=$ and NO_3^-. Their analytical lines of nearly equal relative molar intensities are only 20 cm^{-1} apart, so that the more intense line does contribute significantly to the less intense line. Usually nitrate is in much higher concentration (Table I), and an excellent individual method for carbonate is available. Occasional samples do have higher concentrations of carbonate than nitrate. In such cases, acidification and warming of the sample, followed by neutralization is done to remove carbonate prior to the nitrate determination.

Some waste liquor samples do exhibit other, anomalous spectral interferences. These are apparently due to colloidal particles and are easily removed by filtering.

Advantages to Laser Raman Analysis. The individual methods, which have been employed, typically perform well on standards in a water matrix, but when applied to complex samples of nuclear waste materials that vary widely in composition, analytical performance drops, particularly in a shift type operation. Table III shows standard recoveries and precision for these methods on simple standard solutions. Tables IV and V compare the performance of the individual methods with results obtained by LRS. Precision in all cases is relative standard deviation of a single determination at the 95 percent confidence level. In nearly all cases, accuracy and precision suffers when the individual method is applied to real samples or standards simulating real samples. The two methods to maintain good accuracy and precision are $CO_3^{=}$ by the Oceanography International Corporation carbon analyzer (NDIR), and PO_4^{3-} by spectrophotometry. The laser Raman results indicate better accuracy and precision than the individual methods, with the exception again of $CO_3^{=}$ (NDIR) and PO_4^{3-} (spec) methods.

Of the anions listed in Tables IV and V, $Al(OH)_4^-$ has the poorest precision. There are probably three reasons:

(1) The background is much higher at that portion of the spectrum.

(2) At concentrations exceeding 1<u>M</u> Al, dimerization of the aluminate (5) occurs, resulting in a nonlinear calibration (Figure 4).

(3) Due to the dimerization, sidebands at 540 and 690 cm^{-1} appear, making the aluminate background determination more difficult and inconsistent.

In this work, the background for $Al(OH)_4^-$ was determined by drawing a straight line between 450 cm^{-1} and 760 cm^{-1}. It may be better to accept an even less linear calibration and draw the background from valley to valley on either side of the 623 cm^{-1} band, regardless of the contribution of the two sidebands.

Although no high precision results were obtained by LRS, the precision obtainable has only a low dependence on analyte concentration as indicated by the precision presented for NO_2^-, $Al(OH)_4^-$, and PO_4^{3-} in Table V. At a concentration of about three times the detection limits for NO_2^- and $Al(OH)_4^-$, the precision is only slightly worse than that obtained at concentrations 10-20 times higher. In general, precision is not quite as good as claimed by Marston for the following reasons:

(1) He measured reproducibility of a single peak height measurement as 4.6 percent. Apparently this is not the complete analysis.

(2) His aliquots were larger and thus could be measured more precisely than the 0.1 ml used in this work.

Because of the simultaneous analysis possibilities of LRS for determining oxy-anions, the time required for anion analysis is much less than that needed by individual methods. This is an important advantage. Table VI has tabulated the anion methods and the time required. For five anions, the individual methods require over twice as much time as the Raman method for the same five anions plus sulfate. Automation, which is under development, will further reduce the Raman analysis time by about half.

Another significant advantage to LRS determination of anions in the nuclear industry, is that personnel exposure to radiation is greatly reduced. Sample sizes are small; the minimum quantity in the capillary is a 2.5 mm column or 5 μℓ. The only other aliquot per sample is for the ClO_4^- dilution. Sample preparation time is only a few minutes for determining up to six anions.

Carbonate Methods. Complete data on any carbonate method are not available because the gravimetric method was discarded during the period of data collection in favor of the nondispersive infrared method. The Raman method for carbonate, which is described here, is superior in all ways to the gravimetric method, but still inferior to the nondispersive infrared method (Table V). Consequently, only limited data are available on it, also.

Disadvantages to Laser Raman Analysis. The Raman effect is by nature a weak effect. This gives rise to low sensitivities in analytical methods based on this effect. Table VII shows detection limits for the anions of concern in this work. This is the one area where LRS does not compare favorably with the individual methods of determining these anions. The analytical range for phosphate is also limited on the high side by the solubility of Na_3PO_4 in NaOH solutions.

The low sensitivity makes the Raman methods susceptible to strong optical signals such as fluorescence. Occasional nuclear waste samples do fluoresce, drastically increasing some detection limits. Figure 3 shows a sample spectrum of a waste liquor. The relatively low sensitivity and consequent low peak to background ratio is apparent.

The other major disadvantage is spectral in nature, that of accurately determining background levels for analytical peaks. This disadvantage is greatest for $SO_4^=$ and PO_4^{3-}, where, if the nitrate and chromate peaks are intense, the background is difficult to accurately determine. With automation, peak stripping or peak resolving routines will resolve this difficulty.

The third disadvantage is the chemical requirement that samples be caustic, i.e., that the acids be fully neutralized. Protonation of anions has different effects, depending on the anion. The formation of weak acids, e.g., HSO_4^-, produces different chemical species with an entirely different Raman spectrum, e.g., Irish, et al., studied the effect of pH on the Raman spectrum of $SO_4^=$. Carbonate and NO_2^- anions are lost in acid solutions. This caustic requirement is seldom a disadvantage in our laboratory because nuclear waste materials are highly caustic to begin with.

Samples are not turbid as were those experienced by Marston, but filtering to remove colloidal particles is frequently necessary. This is a relatively minor disadvantage.

CONCLUSIONS

The application of LRS to the determination of oxy-anions in caustic nuclear waste samples provides a fast, reliable method that out-performs most individual methods. The few interferences are mostly spectral in nature. The major disadvantage is low sensitivity, resulting in relatively high detection limits.

ACKNOWLEDGMENTS

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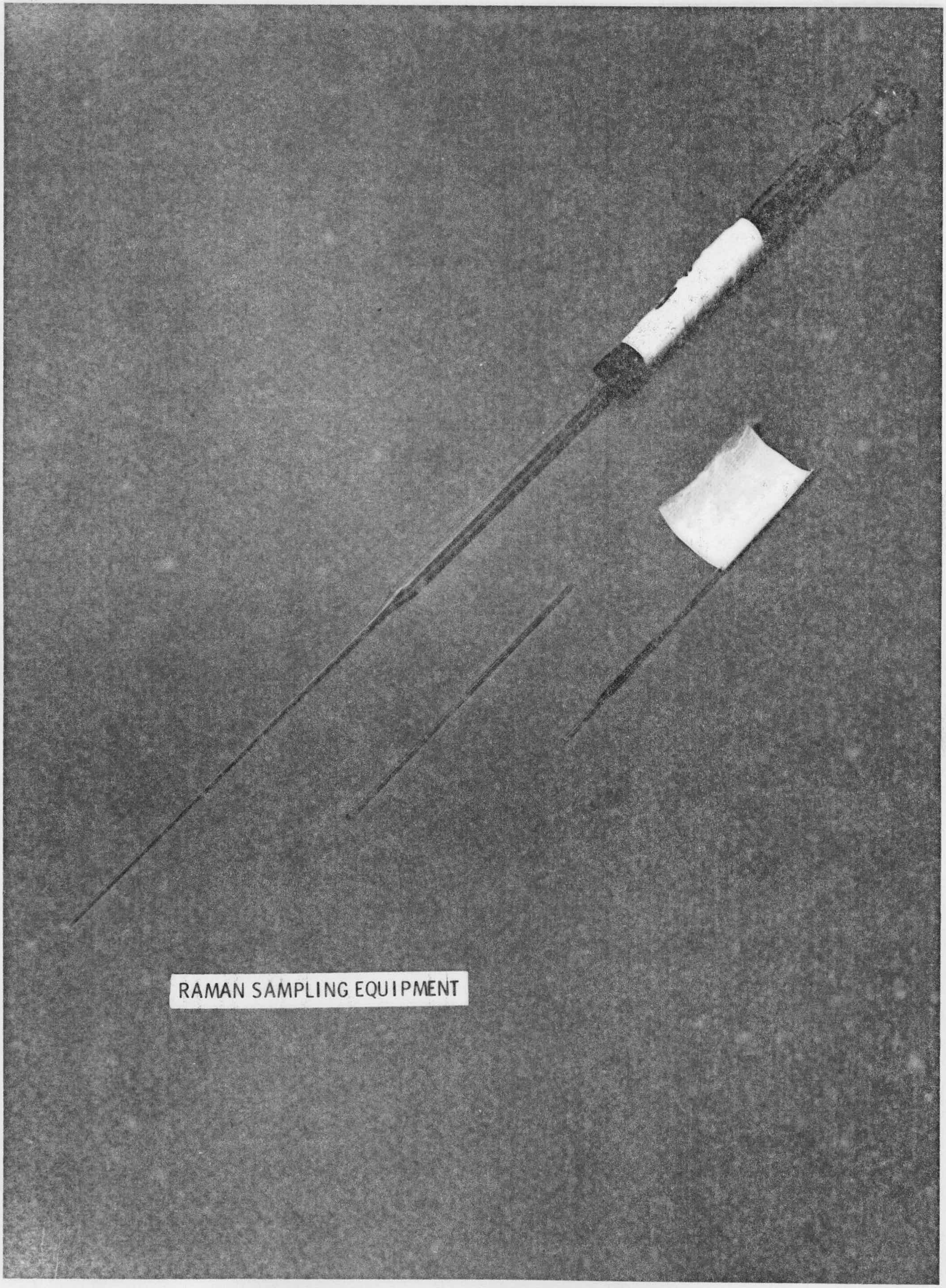

RAMAN SAMPLING EQUIPMENT

FIGURE 2. CO_2 STILL

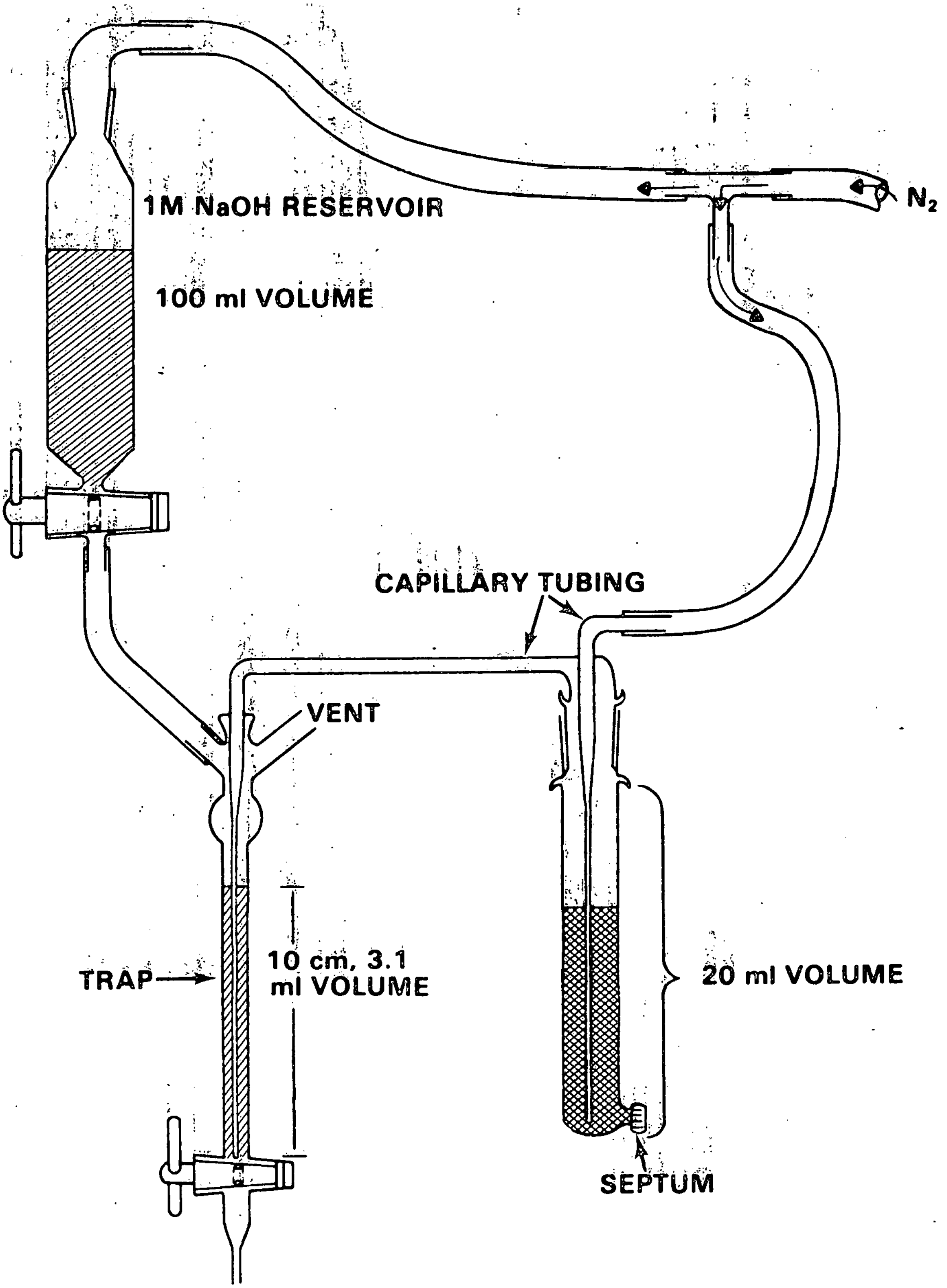

FIGURE 3. SPECTRUM OF WASTE LIQUOR WITH $C1O_4^-$ DILUTION

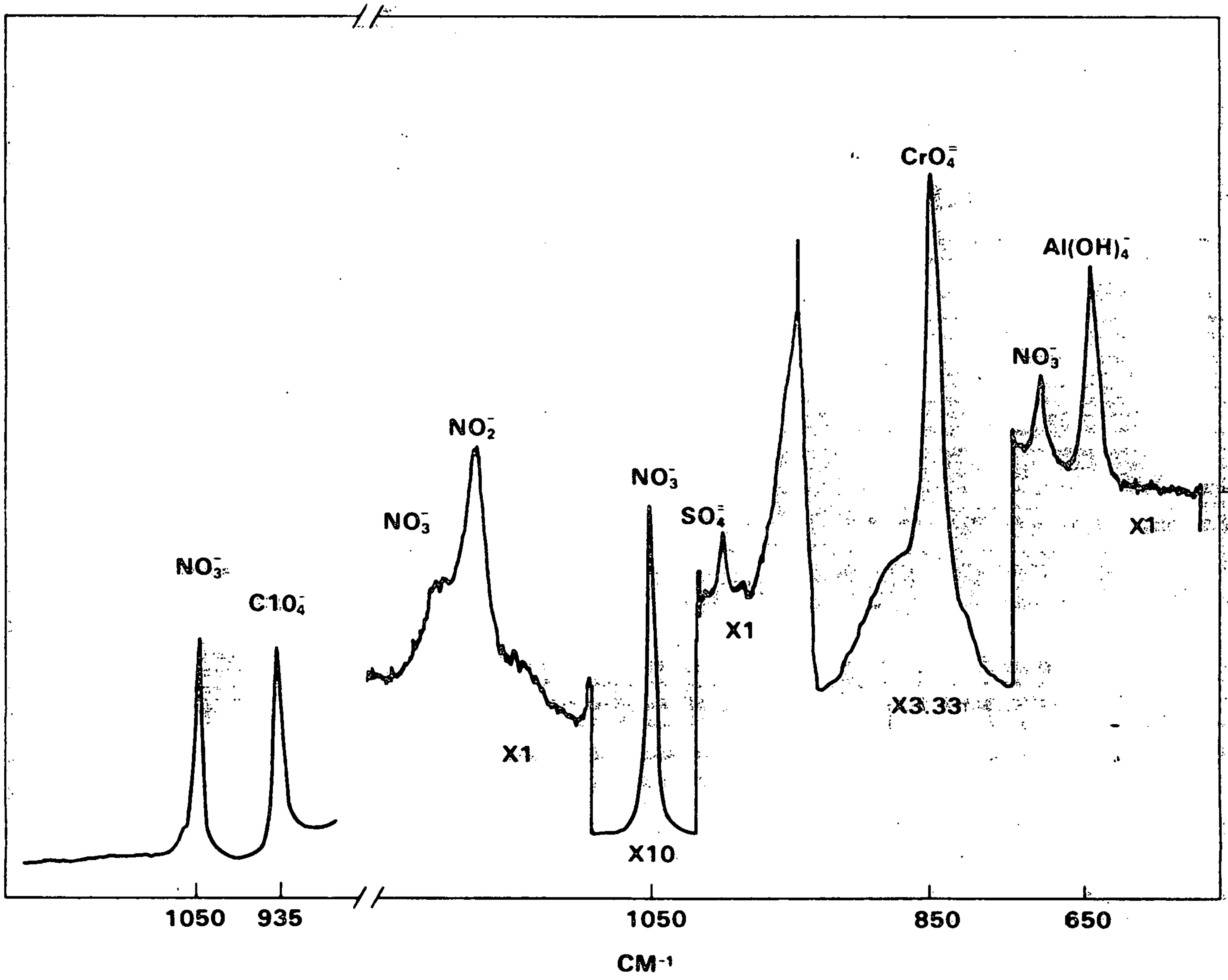

FIGURE 4. CALIBRATION OF $Al(OH)_4^-$

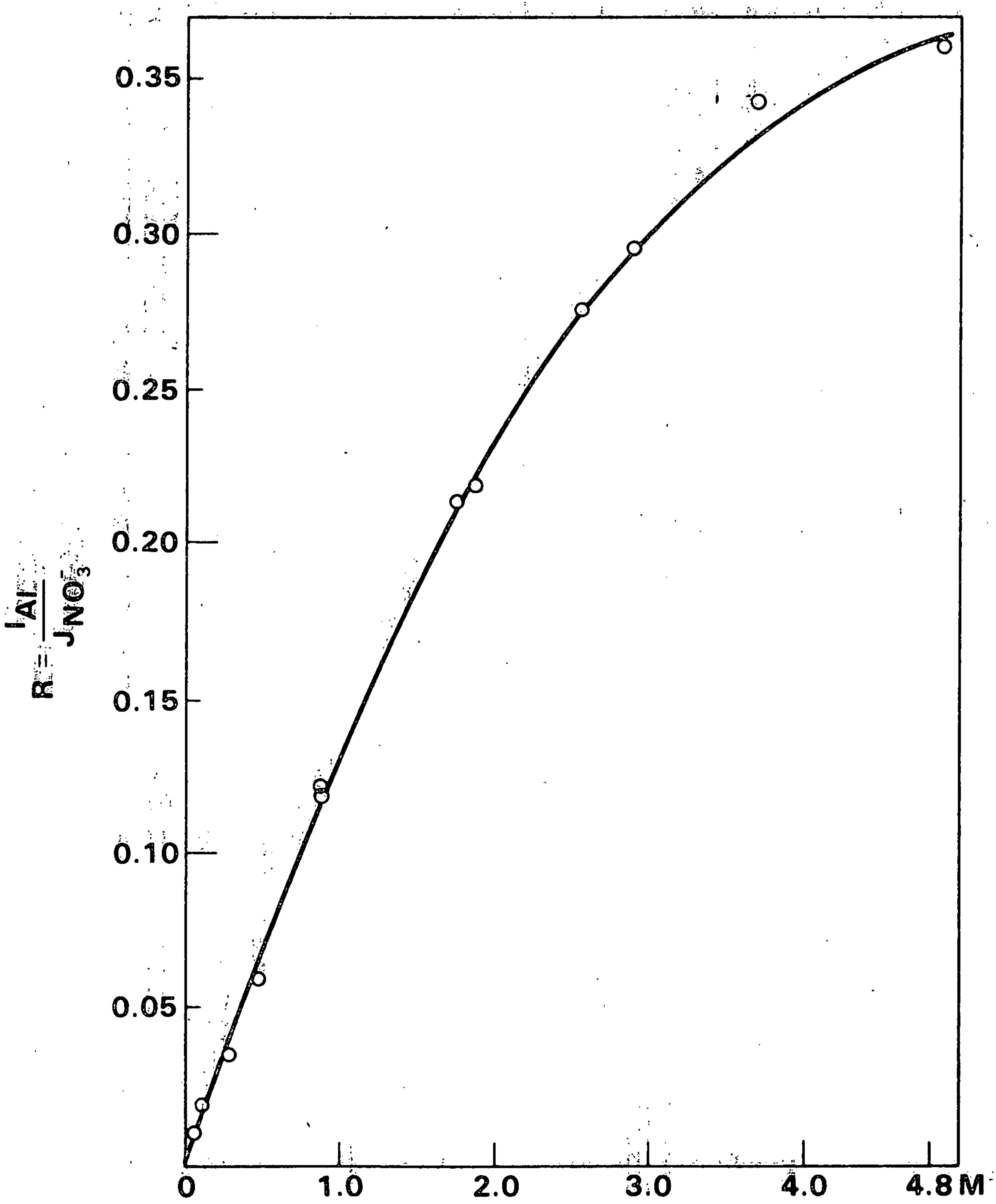

TABLE I. TYPES OF NUCLEAR PROCESSING WASTE

Constituents	Waste Liquor (Molar)	Salt Cake (Wt %)	Sludge (Wt %)
$NaOH$	3.5	1	0.4
$NaNO_3$	2.3	76	3
$NaNO_2$	1.6	1.8	2
$NaAl(OH)_4$	1.6	4	20
Na_2CO_3	0.1	5	5
Na_3PO_4	0.02	2	
Na_2SO_4	0.03	0.4	0.5
Na_2SiO_3	0.002	0.004	2 (SiO_2)
$NaCl$	0.08	0.2	
NaF	0.002	0.001	0.0001
Na_2CrO_4	0.04		
Complexants[a]	0.06		
H_2O	55%	10	34
Ce			0.01
U			0.02
MnO_2			0.7
$Fe(OH)_3$			32
$^{89+90}Sr$	3×10^4 μCi/ℓ	4 μCi/g	500 μCi/g
^{137}Cs	5×10^5 μCi/ℓ	60 μCi/g	200 μCi/g
^{241}Am	5 μCi/ℓ	0.02 μCi/g	0.02 mg/g
$^{239+240}Pu$	3 μCi/ℓ	0.4 μCi/g	2 mg/g

[a] Complexants - Mixture of ethylenediaminetetraacetate, hydroxyethylenediaminetriacetate, and citrate

TABLE II. RELATIVE MOLAR INTENSITIES OF OXY-ANIONS

Ion	Analytical Line cm^{-1}	Relative Molar Intensity[a]	
		Marston	This Work
NO_3^-	1050	1.00	1.000
$Al(OH)_4^-$	624	0.13	0.134
ClO_4^-	935		1.124
$CO_3^=$	1070		0.913
NO_2^-	818	0.055	0.0492
NO_2^-	1330		0.125
$PO_4^{\equiv}$	939	0.16	0.182
$SO_4^=$	985	0.95	1.030
$CrO_4^=$	847	10.	5.76[b]
NO_2^-	818		0.0551[c]
NO_2^-	1330		0.139[c]

[a] Molar intensities relative to nitrate = $\frac{\text{Ion peak height/ion molarity}}{\text{1050 } NO_3^- \text{ peak height/M } NO_3^-}$

[b] Value based on full peak intensity

[c] Intensities measured for NO_2^- in synthetic waste liquor matrix

TABLE III. ANALYTICAL PERFORMANCE OF INDIVIDUAL METHODS ON WATER MATRIX STANDARDS

Constituent	Recovery
Al (ThT)	104±5.6%
Al (AA)	102±17%
$CO_3^=$ (Grav)	96.2±5.1%
$CO_3^=$ (NDIR)	100.7±2.1%
NO_3^- (SIE)	99.5±5.0%
NO_2^- (SIE)	102±1.3%
PO_4^{3-} (Spec)	100.0±5.3%
$SO_4^=$	No method

TABLE IV. COMPARISON OF ANALYTICAL RESULTS ON SYNTHETIC WASTE LIQUOR

Constituent	Individual Method	Laser Raman
1.0M $Al(OH)_4^-$	103±25% (AA)	101.0±11.5%
0.4M $CO_3^=$	106±21% (Grav)	
2.8M NO_3^-	123±16 (SIE)	100.3±6.4%
1.0M NO_2^- (818 cm^{-1})	121±39% (SIE)	104.6±9.9%
NO_2^- (1330 cm^{-1})		101.4±7.6%

TABLE V. COMPARISON OF ANALYTICAL RESULTS ON DISSOLVED SYNTHETIC SALT CAKE (RECOVERIES)

Constituent	Individual Method	Laser Raman
0.040M Al	103±25% (AA)	115±15[a]
0.075M $CO_3^=$	101.2±2.4% (NDIR)	92±8.8[b]
0.032M $CO_3^=$	113±13% (Grav)	
0.0018M $CrO_4^=$	86±16% (AA)	106±8.5
3.02M NO_3^-	113±22% (SIE)	109.3±5.6
0.10M NO_2^-	111±45% (SIE)	117±13[a]
0.042M PO_4^{3-}	108±3.4% (Spec)	90±12[a]
0.014M $SO_4^=$	No method	104.8±6.7

[a] Concentration ∿3X detection limit

[b] Individual method involving chemical separation of $CO_3^=$ from NO_3^-

TABLE VI. TIMES REQUIRED FOR ANALYSIS

Analyte	Method	Hours
Al	AA	0.5
$Al(OH)_4^-$	ThT	0.33
$CrO_4^=$	AA	0.5
NO_3^-	SIE	0.5
NO_2^-	SIE	1.0
PO_4^{3-}	Spec	1.0
$SO_4^=$	--	--
Total, above anions		3.3-3.5
Above anions	LRS	1.5
CO_3^{2-}	Grav	2.0
CO_3^{2-}	NDIR	0.5
CO_3^{2-}	LRS	1.0

TABLE VII. LRS DETECTION LIMITS FOR OXY-ANIONS (IDEAL CONDITIONS)

$Al(OH)_4^-$	0.02<u>M</u>
$CO_3^=$	0.003<u>M</u>
$CrO_4^=$	0.0003<u>M</u>
NO_3^-	0.002<u>M</u>
NO_2^-	0.02<u>M</u>
PO_4^{3-}	0.01<u>M</u>
$SO_4^=$	0.002<u>M</u>