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A SEARCH FOR AN IN-LINE NITRIC ACID ANALYZER

Karin Y. Gallagher

Chemistry Research and Development
PILOT PLANT DEVELOPMENT

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Chemistry Research and Development
INSTRUMENTATION AND STATISTICAL SYSTEMS

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SUBJECT DESCRIPTORS

Nitric Acid
Acid Analyzers

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A SEARCH FOR AN IN-LINE NITRIC ACID ANALYZER

Karin Y. Gallagher and Charles M. Johnson

Abstract. A literature search was conducted to identify possible techniques for measuring mineral acid normality in the presence of heavy metal salts, undissolved solids, and high radiation fields. Of the techniques noted, eight were identified that could be applicable to the objective. The possibilities were reduced to two methods, which warrant further investigation. These two are refractometry and a modified coulometric-polarographic method.

All methods are discussed in detail followed by rationale for including or rejecting each for further investigation.

INTRODUCTION

The analysis of high concentrations of mineral acids in the presence of heavy metal salts is a formidable problem. The objective of this study is the selection of techniques to use in developing an acid analyzer for nitric acid from a continuous dissolver.* The analyzer must meet certain conditions. First, the instrument must operate for periods in excess of six months in high radiation fields and in a corrosive atmosphere. Expected environmental conditions include the following parameters:

Free nitric acid concentration	2.5 to 7N
Uranium concentration	75 to 150 g/l
Plutonium concentration	20 to 50 g/l
Undissolved solids	50 to 100 g/l
Mixed fission products	5 to 15 g/l
Radiation levels	5×10^{10} R

Secondly, the instrument should have the facility of easy replacement.

The literature search conducted on this subject concentrated on, but was not confined to, the nuclear industry and the metal working industry. Two computerized search services were utilized:

the DOE Recon Systems and the Lockheed Information Retrieval Service. The search resulted in the identification of eight methods that could be applied to the objective: refractometry, electrolytic conductivity, ion selective electrodes, modified polarograph, liquid chromatography, ultraviolet analysis, automatic titration, and the Technicon Automatic Analyzer.

This report addresses the feasibility of using each of these methods. The good and the bad points of each method are determined, and an assessment is made regarding the utility of each method for the application just described.

METHODS OF ANALYSIS

Specific Ion Electrode

Semiconductor Electrode

The semiconductor is the anode of an electrochemical cell.¹⁻³ It is operated at a positive potential with respect to a cathode of the material that is inert to the electrolyte. The electrochemical process consists of a constant potential electrolysis and amperometry with the production of a micro-ampere current at a fixed potential. A voltage applied between the semiconductor and cathode produces a measurable current. This current is the result of anodic etching by the electrolyte species. When strong acids are evaluated, the etching process reacts too fast, necessitating dilution of the acid.

Common cathode materials are stainless steel, platinum, and titanium. The semiconductors investigated included germanium, indium antimonide, gallium arsenide, and silicon. Those acids analyzed included hydrofluoric, nitric, hydrochloric, sulfuric, phosphoric, fluoboric, acetic, perchloric, sulfurous, oxalic, citric, tartaric, and sulfanilic. The combination electrode appears capable of measuring acids with K-ion values greater than 1×10^{-6} and slightly lower than that of acetic acid ($K\text{-ion} = 1.75 \times 10^{-5}$).⁴

*This work has been supported in part by a subcontract with Oak Ridge National Laboratory (the ORNL LMFBR project).

When germanium, gallium arsenide, and indium antimonide were investigated, the presence of salts, including oxidizing agents in the electrolyte, interfered with the response of the electrode to acids.^{1,3} Fluoride salts were especially effective in their interference. (They are necessary for all semiconductor electrodes.) Germanium was more sensitive to oxidizing agents than to fluoride salts on an equivalent basis. Conversely, indium antimonide was more sensitive to fluoride salts than to the oxidizing agents, again on an equivalent basis. This interference from hydrolyzable cations cannot be totally eliminated by the addition of complexing or chelating agents.

Silicon electrodes exhibited the best all-around response. N-P and intrinsic types of various resistivities were examined. For the nitric and hydrofluoric acid solutions tested, 0.07 ohm/cm² N-type silicon electrodes could not sustain a stable current suitable for measurement. A maximum resistivity of 0.05 ohm/cm² is necessary.^{5,6}

A silicon electrode is specific for hydrofluoric acid.² Sulfuric and phosphoric acids affects the response of hydrofluoric acid only when the ratios of these acids to hydrofluoric acid are fairly high. Nitric acid, however, produces an enhancement effect for high levels of hydrofluoric acid. This effect is not seriously concentration dependent. To use the silicon electrode for specific acid and total acid concentration analyses; an excess of fluoride salts is needed. Sodium fluoride was tried and it produced a precipitate believed to be Na₃FeF₆ in the presence of iron when in solutions of nitric and hydrofluoric acid. Therefore, the ammonium fluoride salt was preferred.

A full explanation of the effect of fluoride salts on semiconductor electrodes is covered in the Appendix.

Permaplex Membrane Electrode

The permaplex membrane electrode is selective toward the hydrogen ion because of that ion's high mobility.⁵ This electrode has been used successfully for the direct determination of acid concentrations in the $1 \times 10^{-3}N$ -to- $7N$ range.

Two sources of interference have been observed: uncharged molecules and metal cations. Large quantities of uncharged molecules contribute to the membrane electrode potential; small quantities of metal ions cause an interference not exceeding five millivolts. The more highly charged ions produce the greatest interference. Those cations investigated include Cr³⁺, Ni²⁺, K⁺, Ag⁺, and Fe³⁺. In all cases, a preference for hydrogen ions over the metal cations was shown.

Permaplex C-20, a strongly acidic cation membrane containing sulphonic acid groups, was tested. The 0.6-mm-thick membrane was held in place by a polyvinyl chloride body.

An inner reference electrode of silver - silver chloride on a platinum plate with an inner electrode solution of 1N nitric acid and 0.1N hydrochloric acid was used.⁵ The external reference electrode is an Orion Double Junction Reference Electrode.

When compared with a glass electrode, the transference number of the membrane electrode decreased in the range of 0.1 to 7N acid.⁵ In more dilute solutions, 10⁻¹ to 10⁻³N, the transference number was essentially one. Change in the amount of current carried by the electrolyte results in a slight acid error. It is, however, of little practical interest since the measurements are stable.

The electrode will rapidly attain a potential of a few millivolts from its final value, but it takes 2 hr or more before a value stable to better than 1 mV is attained. Long-term stability of the electrode is good; reproducibility is on the order of tenths of a millivolt. This method appears promising for the direct measurement of concentrated acids.

pH Electrode

The concentration of nitric acid can be determined by direct potentiometric comparison of the solution with a set of standards containing known amounts of nitric acid. Measurements are performed with either a glass or quinhydrone electrode against a reference, most commonly the standard calomel electrode.^{4,6} Sample dilution is necessary to bring the acid content to a level suitable for measurement.

Moreover, this will ensure virtually identical ionic strengths for sample and standard.

With a quinhydrone electrode,⁴ a solution of 1M potassium nitrate saturated with quinhydrone is recommended for dilution.¹ For glass electrodes, a solution of 350 g/l ammonium sulfate segmented with air and adjusted to a pH of 5.50 is preferred.⁶ The large excess of ammonium sulfate will act to suppress the hydrolysis of uranyl nitrate. The sample and reagent are mixed in a single coil, passed through a debubbler, and pumped through the electrode flow cell. A hot oil bath will maintain a 95 °C sample temperature.

Low concentrations of uranium and other salts will not disturb the acidity measurements. If the uranium concentration in the monitored solution is higher than 0.2 mol/l, pH measurements are no longer feasible.⁷ With a glass electrode, the precision of an individual result is ± 0.0058 at a nitric acid level of 0.15N.

Electrochemistry

Polarography

Polarography is based on the current-voltage relationship observed at a microelectrode (an electrode having a small area of contact with the solution).⁸ The region in contact with this electrode will differ in composition from the body of the solution. The resulting concentration gradient will produce either a depletion layer (the ions are neutralized on the electrode) or an excess layer (the electrode is ionizing). Under these conditions, the current density at the electrode is determined by (1) the ion diffusion rate through the region of "concentration polarization" and (2) the usual factors of impressed electromotive force, electrode potential, and concentration of the ion in question in the body of the solution. By maximizing the polarization effect, using a microelectrode to measure the desired ionic reaction and a normal electrode to complete the cell, a measure of acid concentration can be obtained. To enhance the polarographic process, an excess of electrolyte inert to electrochemical reaction should be added. This ensures that the diffusion effect of the ion under

analysis is not masked by its role in carrying current through the cell.

A complete description of the polarographic action of the nitrate ion is presented in the Appendix.

Monsanto Nitric Acid Meter

The Monsanto Nitric Acid Meter entails passing an electric current through an aqueous nitric acid solution to produce a selected current density. This density is varied continuously from the maximum.⁹ By discerning resultant, abrupt fluctuations in voltage across the solution, the nitric acid concentration may be determined. In this situation, voltage is a complex, nonlinear function of current density and nitric acid concentration.

Variations in voltage with current density form a hysteresis-type loop. For a selected current density, an abrupt change in voltage may follow a minor change in nitric acid concentration. The point of abrupt increase is more characteristic of nitric acid concentration than the point of abrupt decrease. If the current is varied from high to low or repeatedly interrupted, abrupt rises in the voltage may be discerned. These voltage fluctuations permit accurate determination of nitric acid concentration. This effect is less noticeable at low nitric acid concentrations. Nitric acid can be determined at levels as low as 0.1% nitric acid by weight; however, considerably better results are obtained if the level is above 0.5%. This reduces the effect of secondary influences. A maximum concentration of 75% nitric acid can be detected. To avoid undesirably high current densities, however, a level below 30% (approximately 5N) is suggested.

A continuation of the explanation of this instrument will be found in the Appendix.

Spectrometry

Colorimetry

A colorimetric determination of acid concentration in aqueous solutions, based on the colorimetric reaction with bromocresol green,⁶ was made using a

Technicon Auto Analyzer. The procedure involves suppression of uranyl nitrate hydrolysis by mixing samples with a large excess of $(\text{NH}_4)_2\text{SO}_4$ solution. A 580-m μ filter was used. Results were not entirely satisfactory; the indicator was absorbed on the surface of the analyzer tubing, and when conditions caused the indicator to change from acid to basic or vice versa, false peaks were obtained. The nitric acid concentration was 6N.

A method was developed for determining uranyl nitrate in 1N nitric acid solutions by a colorimetric procedure.⁶ First, nitric acid is segmented with air, and the sample is introduced. Mixing takes place in a double coil. An aliquot of the diluted sample is then pumped through a 15-mm flowcell. A 408-nm filter is used. Data indicated Beer's Law was obeyed throughout the range of intended application. The colorimetric indicator was aqueous thiocyanate. Uranium concentrations of the samples varied from 90 to 75 g/l, and the precision of an individual result was ± 1.3 g/l.

Ultraviolet Analyzer

A deuterium lamp is used as the source of ultraviolet radiation for the ultraviolet spectrometer.¹⁰ Radiation passes through a monochrometer comprised of two ultraviolet interference filters positioned 180° apart on a rotor. One filter has its peak transmission at 300 nm, the maximum absorption wavelength of nitric acid. The second filter transmits at 360 nm, the wavelength of minimal absorbance for nitric acid. The rotor revolves at 3700 rpm, producing a signal frequency of 65 cps. Radiation will traverse the sample cell after passing through the optical filters. Absorption is measured alternately at 300-nm and at 360-nm wavelengths. This makes the procedure insensitive to solids and broadband contaminants in addition to variations in the ultraviolet source and detector elements.

To facilitate measurements, the acid sample is metered into the dilution water stream. A small quantity of the diluted sample (after any necessary treatment for interferences) is diverted to the analyzer. It is recommended that sample and calibration acids be alternated for 10- and 5-min periods, respectively, to allow for detection of instrument failure.

A curve relating nitric acid concentration to absorbance is linear for the range studied (to 0.2N). Variations in signal output were within 5% of the full-scale range over a few hours time.

Visible Range Absorption

Absorption spectrometry will yield a determination of uranium, plutonium, and nitric acid concentrations.⁷ Nitric acid is measured by taking differential variations in the molar extinction coefficients of uranium and plutonium species with variations in the acid concentration. Accuracy is $\pm 5\%$.

Blackening of photo lamps and darkening of the sample cell may be taken into account by splitting a light beam into two parts and passing each through an interference filter. One filter transmits at 416 nm where uranium has a strong absorption band; a second filter transmits at 542 nm where it does not absorb, and light attenuation is due only to interferences. This permits extraneous disturbances to be screened out. Several filters would be needed for the simultaneous determination of several valency levels of uranium and plutonium.

Titration

Iodate and Citrate Titrations

Solutions containing plutonium, thorium, and cerium with known free acid concentrations were analyzed by the iodate and citrate methods.¹¹ In the iodate method, hydrolyzable ions were precipitated with iodate and were separated by filtration. Free acid in the filtrate was then titrated with a standard base. Between 99 and 100% of the free acid in plutonium(IV) solutions and 94 to 96% in plutonium(III) solutions were detected.

Free acid in the preparation of plutonium(III) standard solutions is calculated by subtracting the acid required to form plutonium trichloride from the total acid quantity added. In the iodate method, partial oxidation of plutonium(III) by iodic acid caused a low value. Some oxidation of plutonium(III) also occurred in citrate solutions. These values, however, were high.

Either method, iodate or citrate, will reliably determine free acid in cerium(III) solutions. Both methods produce high results for cerium(IV) solutions. In thorium(IV) analysis, the iodate procedure gives results that agree with the calculated amount of free acid, while the citrate method produces high results (9%). Ammonium ions will cause high results with either method.

High results of the citrate complexing method are attributed to partial hydrolysis of the metal ions present. Another possible interference is from dissolved carbon dioxide in the upper pH range of the citrate titration.

The iodate method is reliable for determining free acid in solutions containing Pu(IV), Th(IV), or Ce(III).

Kolthoff Titration

The Kolthoff ferrous sulfate - dichromate volumetric procedure is an accurate means of determining nitric acid levels.¹² Samples containing from 1.5 to 4% nitric acid (0.2N-0.7N, 25 °C) are mixed with a known excess of ferrous ions in acid solution. The mixture is boiled to remove the oxide of nitrogen formed by reduction of ferrous ions. The remaining ferrous ions are then titrated in the cold solution with dichromate, using ferroin indicator. The ferrous sulfate solution is only moderately stable, necessitating a daily standard. The reactions are

A molybdate catalyst is added to speed up the first reaction. Additionally, the mixture is boiled for 3 minutes to complete the reaction and to expel any NO gas that might interfere. The second reaction occurs readily at room temperatures. At elevated temperatures, the ferroin indicator gives an unstable end point, requiring hot samples to be cooled before running the reaction.

This method has a precision of $\pm 0.4\%$ within 95% confidence limits. It is accurate to within 0.5%, tending to be slightly low.

A proposed shortcut method avoids dichromate titration by requiring titration at 60 °C to the brown color of the ferrous ion-nitric oxide complex. The temperature must be controlled to within ± 3 °C. This method sacrifices much, however, in accuracy and precision while requiring comparable time for completion. It is not recommended.

Organic Phase Titration

A method for determining nitric acid concentration in organic phases, where actinide elements are present, has been proposed.¹³ Titration is performed in the organic phase, and no separations are required. The organic solution studied was a tributyl phosphate mixture with trace amounts of uranium and thorium present. A base, soluble in both the extractant and diluent, was needed. Tributylamine was selected and standardized by titration with perchloric acid in a nonaqueous media. Washing the solution of tributyl phosphate with sodium hydroxide was necessary to remove acidic mono- and dibutyl-phosphates that will react with tributylamine.

A circuit comprised of a glass electrode and a saturated calomel electrode will give stable readings for the acid-base titrations performed on the tributyl phosphate solutions. A voltmeter is used to trace the reaction of the solution, and plotting the titration curve will allow determination of its end point.

This end point deteriorates as the amount of actinides, particularly thorium, are increased. The method can be used in the presence of up to 25 g/l of thorium. Thorium was used to simulate the response of plutonium. The tolerance for plutonium might be increased by oxidizing plutonium(IV) to the less hydrolyzable plutonium(VI), thereby reducing interference. Because of actinide concentration limits inherent in the process, the organic phase aliquots must be diluted.

Liquid Chromatography

Liquid chromatography relies on a packed separation column to selectively retain nitric acid on the packing material surface for a finite period of time.¹⁰ Other

substances pass through unhindered. The detector notes the passage of each species and measures concentration as a function of the respective conductivities. A plot of conductivity versus time will show a peak for each species. The concentration of the species is a function of the area under the peak. For in-line analysis, the system is operated in a semibatch manner. Acid samples are injected into a carrier stream, passed through a metering pump, and fed to the separation column one at a time. From the column, the sample flows to the detector. The detector is essentially an electrical conductivity bridge. Peaks formed for each species are integrated by an electronic integrator. This procedure provides rapid, continuous analyses.

Refractometry

Refractometry measures the phase velocity of radiation in a specified medium relative to radiation velocity in free space.^{14,15} The refractive index will vary with the wavelength of radiation; sodium light of frequency 5893 Å is commonly used. Refractive index provides a nonspecific measurement since refractive indices of the solution components are additive.

Refractometry is a rapid and easy technique requiring only a small volume of the sample. This method is applicable for determining concentration either where only two components are present, the concentration of only one dissolved species is varied, variations in the concentrations of all but one species do not affect the measurements, or independent measurement methods (e.g., pH, density, X-ray, and absorption) are employed in conjunction with refractometry. Where a second measurement method is used, the ratio of coefficients for the index of refraction must differ from the ratio of coefficients for the second property.

The index of refraction of a solution may be expressed in a simple form when only concentration changes are of interest:

$$n_{\text{sol'n}} = n_0 + \sum_{i=1} a_i C_i$$

where $n_{\text{sol'n}}$ and n_0 are the indices of refraction of the solution and pure solvent, respectively, and C is

the concentration in moles per liter of solute. The coefficients of various constituents are nearly independent over small concentration ranges. Neglecting second order terms (they are negligible in the concentration ranges involved), a working equation of the form

$$n_{\text{sol'n}} = n_0 + I_1 C_1 + I_2 C_2 + \dots$$

is obtained. I is the molar refractive index coefficient of the particular species. These molar coefficients will drop as the concentration rises (density coefficients exhibited the same effect); however, they are relatively constant over an appreciable range.

Refractometry is discussed further in the Appendix.

Electrolytic Conductivity

A graph of electrolytic conductivity as a function of acid concentration indicates the curve will pass through a maximum and sometimes a minimum (e.g., sulfuric acid).¹⁶ To facilitate practical measurements, it is necessary to limit the range of the measuring instrument.

There is considerable change in electrolytic conductivity with temperature for a given acid strength. For this reason, accurate temperature compensation must be utilized. Either a temperature-compensating thermistor in the meter or a constant temperature bath would be effective. Heating (or cooling) of the samples will increase (or decrease) the conductivity of a solution, eliminating maximums and minimums from the temperature range of interest. To avoid polarization effects, adequate mixing must be provided. Both an "H"-type cell¹⁶ and an Electrofact electrode¹⁷ were studied.

The discussion of electrolytic conductivity is continued in the Appendix.

Supportive Methods for Nonspecific Techniques

Density

Measurements of density can be used in conjunction with other nonspecific tests to determine nitric acid

and uranium concentrations of a solution. Suggested density meters include one based on the conventional dip-tube method,¹⁷ and an instrument working on either the buoyancy principle or on the flexural oscillation principle.⁷

With the dip-tube density meter, the measured pressure difference is linearly related to the current output. Mixtures containing varying amounts of uranium (200-400 g/l) and nitric acid (0.5-1.5N) were tested. The temperature correction for density was neglected (the temperature coefficient is approximately 0.5 percent per degree Celsius). A relationship for density D (in g/cm³) in terms of acid concentration H (in mol/l) and uranium concentration U (in g/l) was obtained:

$$D = 1.0048 + 0.0311 H + 0.001326 U$$

Total Alpha Activity

Measurements of total alpha activity can be used to determine the concentration of plutonium in the absence of trans-plutonium elements.⁷ Uranium, with a specific alpha activity lower than plutonium by a factor of 10^{-5} , will not interfere. Interference by beta and gamma radiation is reduced by two methods. First, a ZnS screen is used for the alpha detector; beta and gamma particles pass through undetected. Second, the solution is brought under the detector in a thin layer, limiting the activity of beta and gamma particles within the cell. Alpha particles with an activity range of 0.05 mm in liquid are not affected.

Two types of alpha monitors have been tested. For dilute solutions (a fission product activity concentration of 0.2 Ci/l), a weir measuring cell with the detector directly above a shallow trough is recommended. The thickness of the liquid layer flowing through the trough is determined by the weir height. For activities to 50 Ci/l, a drum measuring cell can be used. In this cell, a slowly rotating drum picks up the liquid and brings it under the detector. A Mylar-Teflon foil protects the ZnS screen in both devices from splashes. A dry, warm-air flow prevents fogging of the foil. Slides or disks can be used for calibration purposes. The measuring range is from 10^{-9} to 10^{-2} g/ml. Accuracy is dependent on the isotopic composition of plutonium (this is related

to the burn-up rate). The mid-range measuring accuracy is $\pm 15\%$.

Total Gamma Activity

Measurements of total gamma activity serve to determine the concentration of fission products in process solutions.⁷ Either a scintillation counter or ionization chamber may be used for detection. Plutonium count measurements to 5 $\mu\text{Ci/l}$ give good results; chamber current measurements are recommended for higher concentrations. Extraneous radiation will interfere with measurements. Possible sources include scatter radiation and contaminated cuvettes, pipes, and containers. Lining the cuvette with Teflon will reduce contamination. The measuring accuracy is $\pm 15\%$. Collimators may be used to focus the radiation.

Slides or rotary disks can be used for calibration. Alternatively, a calibration sample may be brought through an isolation lock.

X-Ray Fluorescence

X-ray fluorescence (XRF) works on the principle of bombarding atoms with ionizing radiation of sufficiently high energy to knock electrons out of the inner orbits.⁷ Electromagnetic radiation is emitted when these orbits are refilled from higher electron levels. X-ray radiation is specific for each element. It is identified as either K, L, or M radiation depending on whether the inner shell being refilled is a K, L, or M shell. X-ray spectra have substantially fewer lines than emission spectra, and are therefore particularly suitable for qualitative and quantitative determination of elements. Both dispersive and nondispersive analytical methods are adaptable to the measurement of actinide elements.

X-ray fluorescence is discussed further in the Appendix.

Gamma Absorptometry

When the concentration of uranium and/or plutonium exceeds 10 g/l, gamma absorption is

preferred to nondispersive XRF because of self-absorption interferences.² Gamma absorptometry is based on the attenuation of gamma radiation in its passage through the solution.

The energy of the gamma radiation source should be low enough to ensure that the photo effect predominates over the Compton effect, but it must be higher than the L or the K absorption edge of the element to be detected.

The source nuclide for uranium and plutonium is americium-241 (gamma energy equals 60 keV). The mass absorption coefficients for light elements are so low at this energy that they may be neglected. In a 0.1M nitric acid solution, an error of ± 0.06 g/l is obtained within a measuring range of 10 to 350 g/l. The accuracy is $\pm 7\%$ for an in-line unit.

METHOD EVALUATION

The eight basic methods considered in the previous section will be evaluated as to their potential for application in this project.

To meet the conditions of high radiation and a corrosive atmosphere, the selected method should be simple and, preferably, all major pieces of equipment and electrical components should be located outside the radiation area. Those methods that could be adapted to optical fibers or that use inert electrodes as detectors have the greatest potential. When numerous operations such as dilution, reagent addition, boiling, and mixing are required, the complexity and hence the likelihood of equipment malfunction increases significantly. Moreover, any reagent addition or sample dilution will change the equilibrium of the solution.

Specific Ion Electrode

Three types of specific ion electrodes were investigated. Both the semiconductor and pH electrodes require sample dilution. In addition, an ammonium fluoride reagent is mandatory for nitric acid analysis with a semiconductor electrode. Oxidizing agents and various ions to mask interferences may also be required in the electrolyte. Low

salt concentrations will not interfere in pH measurements, and with the required degree of dilution, the uranium concentration limit of 0.2 mol/l is of no consequence. (For a 7:1 dilution ratio of a sample containing 150 grams of uranium per liter, the analyzed solution will contain only 0.08 mol/l.)

The third specific-ion method, the permplex membrane electrode, appears more promising. Tests have demonstrated its effectiveness in solutions with 7N acid levels. Highly charged ions produced some interference; consequently, further experiments are needed to properly evaluate their significance. Of greater concern is the resiliency of the organic membrane in the high-radiation, corrosive environment.

The semiconductor and pH electrode techniques are not applicable because of sample dilution requirements; any sample conditioning in a remote process is undesirable. Permplex membrane is more nearly feasible but the effects of the high radiation field upon the membrane nullifies its practicability. A continuously fed strip of membrane might overcome this difficulty; however, it would add undesirable complexity.

Electrochemistry

Two electrochemical techniques for nitric acid detection were reviewed. Both relate the current-voltage relationship through an acid solution. Conventional polarography relies on the addition of excess electrolyte to ensure that the diffusion effect predominates over the migration tendency of the ions. The optimum measuring range (5×10^{-5} to $4 \times 10^{-4}N$) would require substantial sample dilution with the attendant equilibrium change. Also, the addition of reagent to counteract metal ion interferences and affect pH adjustment would be needed. The complexity of this method makes it formidable.

The Monsanto nitric acid meter has greater potential. While 5N is the recommended ceiling, it is feasible to extend the ceiling to higher than 12N. Salt interferences are not appreciably significant. As with most techniques, corrections for temperature variation are essential. The detection instrument

consists of two platinum electrodes; these could be placed in a side stream with agitation to prevent polarization effects. All extraneous instrumentation may be located outside the canyon area. This method should be investigated further.

Spectrometry

Several diverse methods involving absorption spectrometry have been considered. All can use optical fibers to control all instrumentation remotely. Colorimetric measurement of nitric acid concentration required dilution of the samples and exhibited problems with the stability of the bromocresol green indicator. This method is not recommended. Uranium detection by colorimetric means was tested with an aqueous thiocyanate indicator in 1N nitric acid for a maximum of 90 grams of uranium per liter. Further investigation would be needed to determine if the analyzer could withstand the pertinent stresses and conditions. The value of the analyzer would be its complementing refractometry or density measurements.

An ultraviolet analysis is a second absorption method for acid concentration analysis. Possible interferences are negated with the use of dual filters. The solutions studied were of much lower acidity (0.2N maximum); however, further investigation might prove this method to be satisfactory.

Absorption spectrometry in the visible range will measure nitric acid concentration and the actinide elements, plutonium and uranium. The accuracy ($\pm 5\%$) is within reason. Further information is needed for evaluation.

Titration

Citrate titrations are unreliable, giving high results. To date, titrations are feasible with plutonium(IV) in solution with concentrated nitric acid. The Kolthoff titration can be applied only with dilute acid solutions. The organic phase titration is not relative to this project. All of the titration methods would require extensive instrumentation that can not be operated remotely.

Chromatography

Liquid chromatography relies on separating nitric acid from compounds in solution through selective retention in a packed column. Assuming the separation could be effected, conductivity measurements would be needed to ascertain acid concentration. As an added detractor, dilution is required. The instrument is too complicated for serious consideration.

Refractometry

The nonspecific techniques of interest are refractometry and electrolytic conductivity. All nonspecific methods would require a corrective technique. This corrective technique is correlated with the primary method through computer calculations. Refractometry is applicable up to an acid normality of nine, does not require sample dilution or reagent addition, and can be remotely instrumented with optical fibers. In conjunction with a second means to distinguish between uranium and nitric acid, it could be an excellent method.

Electrolytic Conductivity

Electrolytic conductivity as a function of acid concentration exhibits maximums and minimums over the broad 2.5N-to-7N range required. Since these maximums and minimums are temperature dependent, dual sample measurements at two or more temperatures might make this concept feasible. However, the required heating baths, metering devices, and additional instrumentation make this concept undesirable.

Supportive Methods for Nonspecific Techniques

Several supportive analytical techniques were considered. Radiation detectors of note are the total alpha monitor and the total gamma activity instrument. Total alpha monitors will detect plutonium in the presence of uranium, but these monitors are of little use for the application described in this report. Measurements of total

gamma activity will determine the total fission product content; however, total gamma counts will not distinguish between plutonium, uranium, and extraneous radiation. The counting accuracy of $\pm 5\%$ is insufficient for the purpose of this investigation.

X-ray fluorescence (XRF) analysis for actinide elements can be either dispersive or nondispersive. Dispersive XRF has high capital and operating expenses and a maximum actinide concentration limit of 30 g/l. Dispersive XRF will not work in this application.

Nondispersive XRF will determine both uranium and plutonium concentration, can be applied to solutions with up to 240 grams of uranium per liter, has low operating costs, and is reliable because of its simple electronics. It might be useful in conjunction with refractometry or density measurement.

Gamma absorptometry is preferred over nondispersive XRF for uranium and plutonium detection. It has fewer interferences and can be remotely instrumented. Also, it can be applied in solutions with up to 350 grams of uranium per liter. Again, its potential lies as a secondary detector for use with refractometry or density measurement.

Density measurements are straightforward, exhibiting a proportionality between measured values and concentrations of nitric acid and uranium. Any one of several methods will provide simple instrumentation. Measuring both refractive index and density could produce results of sufficient accuracy and precision with a minimum degree of complexity.

Alternatively, either density or refractometric measurements could be combined with a means of uranium detection, should the density-refractive index determination prove faulty.

CONCLUSIONS

The two methods with the greatest promise are the Monsanto nitric acid meter, and a combination of

refractometry and density measurement. Several methods for uranium detection are possible and might prove useful with either refractometry or density monitoring.

Further laboratory investigations are warranted to establish operational parameters and feasibility for this application.

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APPENDIX

Semiconductor Electrode

The explanation of the effect of fluoride salts on semiconductor electrodes is as follows.

The addition of NH_4F accomplishes three objectives.² First, it produces a weakly ionized molecular species, HF , by forcing the equilibrium in that direction; e.g., with nitric acid,

The electrode responds only to hydrofluoric acid or fluoride ions in acid solution and is not influenced by the changing ionic strength of the salts.

Second, excess fluoride is required to produce current and saturation. A current amplification factor of four is obtained for hydrofluoric acid in the presence of excess fluoride. This suggests the anodic etching mechanism for silicon may involve the HF_2^- anion:

Beyond 2 g NH_4F per 200 ml of electrolyte, the law of diminishing returns applies (for the studied electrode sizes and acid concentrations).

Finally, excess NH_4F forms fluoride complexes with cations, which normally hydrolyze to produce acid. With ferrous ion,

instead of

These fluoride complexes are more stable than the corresponding hydroxy complexes for the applicable pH values. This enables the determination of free acid in the presence of cations that hydrolyze

spontaneously. Additionally, this phenomena reduces film formation at the electrode. Iron, chromium, nickel, titanium, manganese, molybdenum, vanadium, and silicon complex with fluoride where possible (Ni^{2+} , Fe^{2+} , and Mn^{2+} do not normally form complexes with fluoride). No interference from these complexed fluoride salts was apparent.

Metals in high oxidation states exhibit a reduction effect that produce readings approximately 5% higher than normal. Particularly susceptible is Cu^{2+} . Also exhibiting this effect are Zn^{2+} , Cr^{3+} , Fe^{3+} , and UO_2^{2+} . The copper ions, Cu^{2+} , are not appreciably concentration dependent and can be screened out by adding the reducible ion to the NH_4F calibration electrolyte. Metallic ions in their lowest stable oxidation state in an aqueous medium produce little or no interference for silicon electrodes. These ions include Al^{3+} , Fe^{2+} , Ni^{2+} , Mn^{2+} , Pb^{2+} , Zn^{2+} , Ti^{4+} , and Mo^{6+} .

The addition of an oxidizing etchant produces a 50% increase in response. The commonly used oxidizing agents are hydrogen peroxide, potassium dichromate, potassium permanganate, and ammonium persulfate. Oxidizable cations consume hydrogen ions in the presence of an oxidizing etchant; consequently, the use of oxidizing agents must be avoided in their presence. Fortunately, ammonium fluoride alone will give good data. Ammonium persulfate is a possible exception; it does not consume hydrogen ions in the presence of ferrous ions.¹

Stronger acid solutions improve sensitivity and eliminate metal ion interference, thus creating a dependence on the acid normality for the response. The water-soluble organic acids, citric and oxalic, give a weak response in reference to silicon. Sulfanilic and tartaric acid give a strong response.¹

The silicon-electrode measuring range extends from 0.001 to 0.05N acid following dilution. Those anodes tested had areas ranging from 2.5 to 6 cm and were recessed in the cathode tube. Each cathode tube had a polyvinyl chloride cap with

holes 0.238 cm (3/32 in.) in diameter drilled around the outer circumference 1.58 cm (5/8 in.) apart. The holes prevent air lock while providing dark surroundings for the anode. Electrodes of a smaller area allow higher acid concentrations for a given current reading. Small electrodes also exhibit a lower overall temperature effect.

Three methods exist for neutralizing the temperature dependence of response for silicon electrodes:

1. temperature compensator
2. constant temperature water bath for dilution
3. temperature calibration curve and daily standards to correct for temperature variations

In summary, the response of an electrode is influenced by its area, electrical potential, electrode resistivity, type (N, P, or intrinsic), dislocation density, and crystal orientation. There is also some evidence to suggest that the element dopant for a given resistivity and type will influence the current response.

Equilibrium can be attained in one minute. The data are not quite linear, but they are reproducible. Electrode wear from etching has not proven to be a problem (three-year-old electrodes were fully functional). Care must be taken in handling the semiconductor anode as it is brittle and sensitive to light.

Polarography

The dropping mercury electrode meets the prerequisites for producing a polarization effect. Its size, a forming drop of mercury, is sufficiently small. Furthermore, it possesses the advantage of constantly being replaced; deposits can not form on its surface, contributing unwanted polarization effects. A standard calomel electrode is recommended to complete the circuit.

The reduction of nitrate has been observed at the dropping mercury electrode in the presence of large excesses of lanthanum, or small amounts of uranyl ion.⁸ The nitrate wave appears at a more positive potential and is more normal in appearance

than that observed in the presence of lanthanum. Furthermore, the nitrate wave is subject to less interference by other anions.

In moderate concentrations of hydrochloric acid (0.001 to 0.01*N*), uranyl chloride gives three uranium reduction waves. When nitrate is also present, the nitrate is reduced at potentials where the second uranium wave occurs. The half-wave potential of the nitrate wave is approximately -0.9 to -1.0 V (versus standard calomel electrode) with a supporting electrolyte of 0.01*M* KCl, 0.01*M* HCl, and 2×10^{-4} *M* uranyl chloride.

Lanthanum chloride was found to produce a nitrate diffusion current proportional to the nitrate concentration. The diffusion current in the presence of nitrate was proportional to the nitrate concentration, when the ratio of uranyl to nitrate was above a minimum. The minimum ratio is dependent on the nitrate concentration, decreasing with increasing nitrate levels. Below this minimum, the nitrate diffusion current ceases to be proportional to the nitrate concentration. The proportionality holds for large excesses of uranyl, but the "residual" current due to the reduction of the uranyl ion increases, making measurements of the nitrate diffusion current less accurate. For solutions of 0.01*M* KCl, 0.01*M* HCl, and 2×10^{-4} *M* uranyl chloride containing varying amounts of potassium nitrate, the optimum concentration range is 5×10^{-5} to 4×10^{-4} *M*.

The reduction of nitrate under the described conditions involves five electrons, indicating a reduction to nitrogen. This high electron consumption allows the quantitative determination of very dilute nitrate solutions.

The laboratory procedure requires the addition of a uranyl chloride electrolyte to the sample, followed by bubbling to ensure that no air is entrained in the solution. Additional reagents may be necessary depending on interferences present. Adjustment of the pH is often needed. Basic solutions will precipitate uranium while highly acid solutions (greater than 0.1*N*) cause the reduction of hydrogen before -1.2 V. The addition of a methyl red indicator, sodium hydroxide, and hydrochloric acid will allow the acidity to be adjusted.

Sulfate, oxalate, and phosphate are three common sources of interference. Sulfate will interface only when greatly in excess to nitrate. In such instances, it can be precipitated through the addition of strontium sulfate. In the presence of uranyl, oxalate is reduced at the same potential as nitrate and must be removed. Phosphate will precipitate uranyl, necessitating its removal. Uranyl also can be precipitated with alkali-earth metals. Additionally, any substance present in large amounts, which gives a reduction wave before the nitrate wave, will interfere and should be removed, e.g., copper and lead.

Uranous sulfate demonstrated the same catalytic effect on the nitrate reduction as uranyl chloride. However, uranous sulfate solutions are oxidized by air. Hence, the use of stable uranyl chloride solution generally is preferred.

In addition to its use for nitric acid determination, polarography has produced good results in monitoring small concentrations of uranium.⁷ The error is $\pm 10\%$ in the range of 0.02 to 10 grams of uranium per liter. Cations that are reduced at more positive potentials than uranium (Ce^{4+} , Fe^{3+} , and Pu^{4+}) will interfere. The addition of ascorbic acid reduces these to polarographically inactive valency levels.

An interference that cannot be eliminated is the fission product $(\text{RuNO})^{3+}$. This product reduces the diffusion potential of hydrogen as the mercury drops. More than 10^{-3} mol/l of this ion makes polarography impossible.

When tributyl phosphate is dissolved in the aqueous solution, the uranium reduction diffusion current is reduced by a constant amount. The resulting error can be taken into account by calibration.

In addition to ascorbic acid, the destruction of nitrite ions present in solution requires the introduction of a methanol reagent.

A proposed system for the continuous monitoring of uranium requires a diversion stream that is pumped to a metering vessel. From there it passes to a preparation vessel where methanol-containing ascorbic acid is introduced, and de-aeration is accomplished by flushing the solution with nitrogen.

Finally, the solution is admitted to the polarography cell for measurement of the uranium concentration. Ten-minute cycles are anticipated. The expected standard deviation is $\pm 2.2\%$.

Monsanto Nitric Acid Meter

Secondary hydrogen ion sources will not affect the accuracy of readings and can be advantageous. Water concentration in the bath should be in the 1-to-90 wt % range with 10 to 60% preferred for reliable measurements. Sufficient water is needed to make the bath electrically conductive, but not to an excess where undesirable low current densities are required. Any secondary hydrogen source constituting one or more acidic substances (phosphoric and sulphuric acids are two commonly encountered) that will reduce the water content below the 90% maximum dash (preferably below about 45% or even 25%) would be desirable.

Inorganic salts do not appreciably affect the results. The abrupt voltage rise is still noted. However, with high salt concentrations, slight corrections may be required. In addition to salts and acids, the bath can satisfactorily contain any material that does not react at an undesirable rate with nitric acid and is reasonably stable in its presence.

Measurements should be made on hot samples. The lower the nitric acid level, the hotter the sample should be for accurate instrument response. Temperatures in the 80-to-120 °C range are recommended; a 100 °C temperature is preferred. Below 60 °C, low current densities make measurements impractical. A change of 1 °C in temperature produces a 0.47% change in the measurement of nitric acid. To maintain the temperature level, a hot water bath could be employed to quickly equilibrate samples.

Stirring of the samples is essential to prevent polarization effects. Magnetic stirring would be suitable because it is difficult to overdo, thereby aerating the sample. Some added precautions may be necessary to prevent evaporation.

Current is controlled by varying the exposed area of the cathode. The cathode should be of sufficient

size that the current can be readily measured, but not so great as to require an excessively long period to liberate the hydrogen that is dissipated from the cathode. Cathode areas must fall within the 0.01 to 10 A/cm² of the cathode area range. Limiting the variation to 0.1 to 2 A/cm² is recommended.

The current density is measured between two platinum electrodes. Gold or one of the noble metals would also be a suitable electrode material.

The measurements can be performed directly in the acid bath; however, this requires exposing the meter to a severe environment. The Kolthoff titration procedure is recommended for calibrations and checks.

Refractometry

As a first approximation, the volume percent of solute in a two-component system is related to the indices by the formula

$$\text{vol \%} = 100 \times \frac{n_{\text{sol'n}} - n_0}{n_1 - n_0} = \frac{100 \Delta n}{n_1 - n_0}$$

where $n_{\text{sol'n}}$, n_0 , and n_1 are, respectively, indices of the solution, pure solvent, and pure solute.

The molar index coefficient is given by

$$I_1 = \frac{\Delta n}{\text{mol}_1} = (n_1 - n_0) \frac{V}{10^3}$$

where V is the molar volume of the solute.

For organic solvents, tributyl phosphate (TBP) and Amsco 125.90 W have nearly the same index of refraction. Thus, the coefficients are independent of the volume percent TBP in the diluent. Also, the molar coefficient for nitric acid in an organic solvent is small. This is a disadvantage when the acid to be analyzed is not a major constituent.

The wavelength of the sodium D line is used as a reference in measuring uranyl nitrate solutions. For theoretical reasons, a rapid increase in the index of refraction for uranyl nitrate is expected as the wavelength is lowered towards the violet end of

the spectrum. This increase was found to be smaller than predicted and does not compensate for the greater difficulty of observing blue-violet light as opposed to sodium's yellow.

For experiments performed at 25 °C, the relationships between refractive index (n), uranium concentration $[U]$, and nitric acid concentration $[HNO_3]$ are $(n/U)(1/HNO_3)$ for aqueous systems, and $(n/U)(\log HNO_3)$ for organic solutions.¹²

In aqueous systems,

$$n = k_1 [U] + k_2$$

$$k_1 = (146.6 - 5 [HNO_3]) \cdot 10^{-6}$$

$$k_2 = 1.3324 + 7.52 \cdot 10^{-3} [HNO_3]$$

where U is in grams per liter and HNO_3 is in moles per liter. The constants k_1 and k_2 depend upon the nitric acid concentration $[HNO_3]$. The expression for k_2 is valid for concentrations up to 4N nitric acid. The value "1.3324" is the refractive index of water at 25 °C. The term for the molar refractive index coefficient for uranium, k_1 , is dependent on the concentration of nitric acid. For the specified restraints, the expression for refractive index is

$$n = (146.6 - 5 [HNO_3]) \cdot 10^{-6} [U] + f([HNO_3]) + 1.3324$$

In organic solutions,

$$n = k_1 [U] + k_2$$

$$k_1 = (92.3 + 11.4 \log [HNO_3] \text{ aq}) \cdot 10^{-6}$$

$$k_2 = 1.4187 - 19.8 \cdot 10^{-4} \log [HNO_3] \text{ aq}$$

The nitric acid (HNO_3 aq) must be the same for all samples. The quantity "1.4187" is the refractive index of the pure solvent (tri-*n*-butylphosphate/doedecane mixture). The molar refractive index coefficient for uranium is, again, dependent on the HNO_3 in the aqueous phase. The complete expression for refractive index is

$$\begin{aligned}
 n = & (92.3 + 11.4 \log [\text{HNO}_3]_{\text{aq}}) \\
 & \cdot 10^{-6} \cdot [\text{U}] - 19.8 \\
 & \cdot 10^{-4} \log [\text{HNO}_3]_{\text{aq}} \\
 & + 1.4187
 \end{aligned}$$

Abbe-type refractometers display a constant reading error equal to 0.0001 refractive units. This is attributed to (1) inaccuracy in measuring the acid concentration, (2) the presence of colloidal particles, (3) temperature differences, and (4) changes in light composition. To obtain an error of the same order as the reading error in the calculations, the nitric acid concentration must be controlled to within 0.01N. The method is preferably applied to higher uranium concentration ranges (40 g/l minimum).

Concentrations up to 300 grams of uranium per liter in aqueous media, and 120 grams of uranium per liter in organic solutions can be measured.¹⁵ The nitric acid concentration of the aqueous phase should not exceed 9N. The refractometer is sensitive to 1 gram of solute per liter for the aqueous phase, and 1.1 grams of solute per liter for the organic phase. Dilute solutions cannot be adequately measured.

Electrolytic Conductivity

The "H"-type conductivity cell embodies two conducting electrodes through which a small alternating current can be passed. A thermistor located against the inside of the cell wall provides temperature compensation. The cell consists of a platinum electrode assembly over which side tubes are fitted. This extends the electrical path between the electrodes. The tubes are held parallel by disks when the cell is inserted in its housing. The disks, being slightly smaller than the housing, cause the major portion of the flow to pass through the side tubes and directly past the electrodes. This reduces measurement time lag while purging the electrodes of contaminants and gas bubbles. Secondary components include the electrical circuits, amplifiers, and receiving instruments for indication, recording, transmission, and control. This method can be used in acid concentrations as great as 90 wt % HNO_3 (20N at 25 °C).

The Electrofact electrode (cell type 50011, range box type 33240, transmitter type 43200 with 3000 Hz oscillator) was equipped with temperature compensation. The determination of temperature coefficients for the relevant concentrations was necessary. Uranium concentrations varied from 200 to 400 g/l, and nitric acid varied from 0.5 to 1.5N. Conductivity ranged from 0.1 to 0.3 mho/cm². An equation was obtained for the selected instrument relating conductance (1/R mho) and current output [I(mA)]:

$$\begin{aligned}
 \log 1/R = & 2.316 + 0.03238 I \\
 & - 0.0001762 I^2
 \end{aligned}$$

For a cell constant 10 mho/cm², the conductivity (K) can be calculated from

$$\log K = \log 10 + \log 1/R$$

Temperature coefficients, TC, are represented by

$$\begin{aligned}
 \text{TC} = & 1.8 - 0.5 A + 0.0004 U \\
 & + 0.0014 AU
 \end{aligned}$$

where A is the acid concentration in moles per liter, and U is the uranium concentration in grams per liter. Regression analysis gave a relationship for conductance:

$$\begin{aligned}
 K = & 0.0959 + 0.1983 A - 0.0000183 U \\
 & - 0.000336 AU
 \end{aligned}$$

From the equation it can be seen that conductivity decreases with increasing uranium concentration in the region studied. This indicates an interaction term is required in describing measurements.

Conductivity is a nonspecific measurement; its value lies with measurements where only two components affect conductivity, or when used in conjunction with other nonspecific methods.

The accuracy depends on the solution composition and may vary between ± 4 and $\pm 10\%$ (in conjunction with density measurements).⁷ A precision of 1% is predicted for the Electrofact electrode.¹⁷

Other methods involving no electrodes may be better suited for measurements of nitric acid and uranium concentrations.⁷

X-Ray Fluorescence (XRF)

In dispersive XRF, the tubes used for excitation of the characteristic X-ray lines are equipped with a tungsten cathode. Radiation is selected by dispersion in an analyzer crystal. As this entails high radiation losses, the intensity of the X-ray tube must be high, corresponding roughly to an activity in the kilocurie range. Therefore, operating and capital costs for such a system are also high.

The high spectral parity of the exciting radiation, in conjunction with the high energy resolution, will allow the determination of neighboring elements side by side. The emission line is used for in-line analysis of uranium and plutonium in aqueous or organic phases. The allowable actinide concentration range is 0.015 to 30 g/l. In the cuvette, fission product activities to 8 mCi/l and corrosion product concentrations to 1 g/l will not disturb measurements. A multichannel X-ray spectrometer (Siemens) allowing for simultaneous measurements on a maximum of seven channels is suggested.

Nondispersive XRF uses excitation of the characteristic fluorescent radiation by radionuclide sources and energy resolution by pulse height analysis. Three distinct advantages are inherent in this method:

1. high efficiency — a source activity in the millicurie range is adequate
2. high reliability owing to the simplicity of the electronics
3. low operating costs

The disadvantages are poor energy resolution and relatively high detection limits.

Three alternatives are feasible for the detector: proportional counter tubes, semiconductor

detectors, and scintillation counters. If the energy resolution is poorer than 0.66 keV, the L_I line will determine uranium and plutonium jointly. Differential filters will be needed to achieve separation.

Radiation sources for X-ray fluorescence are monoenergetic gamma emitters that involve energy levels slightly higher than the excitation energy of the element to be determined. This avoids excessive background radiation. Low-energy (60 keV) beta radiation is also of interest because of the brems radiation spectrum that it generates.

Utilization of beta emitters can be improved substantially by the intercalation of intermediate targets excited to emit characteristic X-ray lines. The intermediate targets used in uranium analysis should have characteristic X-ray energies only slightly higher than the L_{III} edge of uranium (17,163 keV). Owing to its favorable energy level, molybdenum is particularly suitable for the selective determination of uranium. However, because of the emission energy of molybdenum (17,478 keV) being lower than the excitation energy of plutonium (18,066 keV), plutonium is not detected.

The half-lives of the radionuclides used as sources should be sufficiently long to ensure a reasonably constant radiation intensity.

The measuring range of nondispersive XRF is limited by background radiation and self-absorption effects. The use of Se-75 for K excitation reduces self-absorption, extending the measuring range to higher concentrations. The uranium measuring range with K excitation extends from 10 to 240 g/l with a standard deviation of 1%.

A suggestion for in-line uranium determinations is use of a continuous flow-cell consisting of a thin-bottomed Plexiglas cuvette in conjunction with a radiation source comprised of either americium-241 or nickel-63, and a molybdenum intermediate target. A detector consisting of either a xenon proportional counter tube or an X-ray scintillation counter with a thin sodium iodide crystal is preferred.