with an ICP system). Based on background emission spectra, the side-on arrangement was judged superior.

The potential of this system for chemical analysis is readily seen in Fig. 13. Under the optimum operating and optical viewing conditions, 10 ng/mL of lithium and 100 ng/mL of potassium are easily detected. The zero (0) level marker indicates the magnitude of the dark-current contribution from the PMT. This spectrum also shows that there is essentially no background continuum emission to affect measurements at these wavelengths. The present study shows the MINDAP system to be a sensitive emission source for elemental analysis. In a companion paper[29] it is critically evaluated from its analytical figures-of-merit.

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Atomic Absorption Determination of Titanium and Vanadium in Uranium Concentrates

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An atomic absorption procedure was developed for the determination of titanium and vanadium in medium-purity uranium products (yellow-cakes). Samples equivalent to 4 g uranium were dissolved in 5.5 M nitric acid. Titanium and vanadium were separated from the uranium matrix by column extraction chromatography with the use of tri-*n*-butyl phosphate (TBP) supported on polytrifluorochloroetylene (Kel-F)® powder. A nitrous oxide-acetylene flame was employed to estimate the concentration of the analytes in the nitric phase. The precision was about 3% relative standard deviation for both elements, with detection limits of 60 μg/g for Ti and 30 μg/g for V. The influence of Al, Fe, and PO_4^{3-} on the measured absorbance values and mutual interferences effects between Ti and V were investigated.

Index Headings: **Atomic absorption spectrometry; Titanium; Vanadium; Extraction chromatography; Uranium concentrates.**

INTRODUCTION

The estimation of metallic impurities in uranium concentrates, commonly known as "yellow-cakes" and composed mostly of ammonium diuranate, is necessary because of their use as raw material for production of nuclear fuels. Titanium and vanadium are usually not considered as critical nuclear poisons. However, rather low concentrations of these elements are required in order to decrease the cost of subsequent purification stages.

Titanium and vanadium can be determined in uranium products with the use of several spectrophotometric methods[1] or by dc arc emission spectrography after chemical separation and concentration.[2,3] Atomic absorption spectrometry has also been used by several authors for estimation of trace elements in uranium compounds.[4–6] Liquid-liquid extraction with tri-*n*-butyl phosphate is usually employed to separate the uranium

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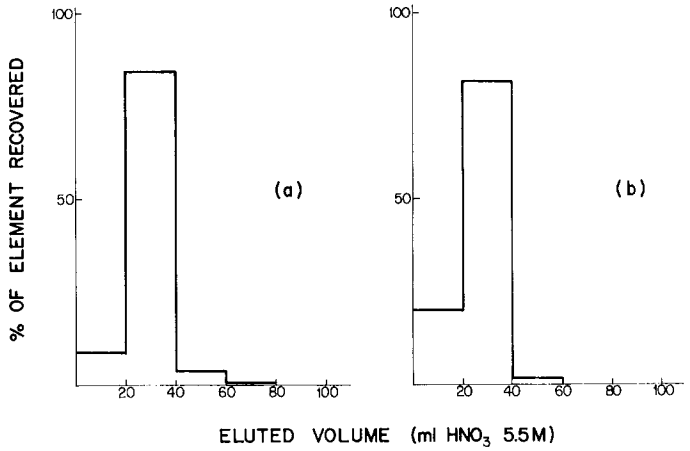

FIG. 1. Elution of titanium and vanadium with 5.5 M nitric acid; (a) Titanium; (b) Vanadium.

because of radioactive contamination problems and the poor sensitivity observed for the direct determination.

The removal of uranium has also been performed by extraction chromatography by Hayes and Hamlin[7] and by Fletcher, Franklin, and Goodall,[8] who determined several elements in a nitric acid solution, free of uranium, that was eluted from a chromatographic column, by spark emission spectrography. A similar separation method was employed by Pagliai and Pozzi[9] to analyze solutions of highly enriched uranium by atomic absorption.

The present paper describes the separation of titanium and vanadium from uranium concentrates by column extraction chromatography, with the use of polytrifluorochloroetylene (Kel-F)® as a support and tri-*n*-butyl phosphate (TBP) as a stationary phase. Both elements are eluted with 5.5 M nitric acid and subsequently determined by flame atomic absorption spectrometry.

EXPERIMENTAL

All chemicals and reagents were of analytical grade. Stock solutions of Ti and V 1000 μg/mL were prepared from Titrisol (Merck). Bidistilled water was used throughout. Standard solutions containing 2000 μg/mL K and 300 μg/mL Al, with varying concentrations of Ti and V were prepared in 5.5 M nitric acid.

Kel-F® powder (20–70 mesh) was obtained from Minnesota Mining and Manufacturing Co., Minneapolis, MN. For chromatographic separation, a glass column 25-cm-long, 1.7-cm-i.d., was employed. The column was filled with TBP. Kel-F® powder was added until the bed length reached about 23 cm. After the support was completely saturated, excess TBP was drained and the column thoroughly washed with water and then saturated with 5.5 M nitric acid.

Uranium concentrate samples equivalent to 4 g of U were dissolved in nitric acid, evaporated to almost dryness, and redissolved in a minimum volume of 5.5 M nitric acid. We filtered this solution (if necessary), washing with 5.5 M nitric acid, and the filtrate was poured through the column. The elution flow rate was regulated at about 2 mL/min. The uranium was retained by the adsorbed TBP, and Ti and V were eluted with 5.5 M nitric acid, collected in a 100-ml volumetric flask containing 3 mL of aluminum chloride solution (Al 10 mg/mL) and 2 mL potassium chloride solution (K 100 mg/mL). The uranium was subsequently eluted with water. After about ten separations, we conditioned the column by draining off the aqueous phase, adding a few mL of TBP, and washing thoroughly with water.

TABLE I. Effect of small area measurements on Ti absorbance.

Ti concentration μg/mL	Absorbance		
	Conventional measurement	Small area measurement	% Variation
10	0.016	0.022	+38
50	0.049	0.068	+39
150	0.132	0.179	+36

A Jarrell-Ash model 82-500 atomic absorption and emission spectrometer, with single-element hollow-cathode lamps and a grooved titanium burner for nitrous oxide-acetylene flame was used in these experiments. Analytical wavelengths were Ti: 365.35 nm and V: 318.40 nm. A hydrogen hollow-cathode lamp was employed for background absorption measurements. Flame conditions are described in the next section. Absorbance readings were made with a Fluke 8086 digital multimeter and recorded with a strip card recorder. The analytical calibration curves obtained covered the range 10–150 μg/mL for Ti and 20–200 μg/mL for V.

For absorption measurements over a small area of the flame, a plate with a 2-mm circular pinhole was interposed between the lens near the monochromator and the monochromator slit. The entrance slit height was reduced to 2 mm.

RESULTS AND DISCUSSION

Chromatographic Separation. Preliminary tests showed that the chromatographic separation of Ti and V should be performed on sample sizes equivalent to 4–5 g of uranium. Those amounts of uranium were easily retained by the column without appreciable uranium tailing.

In order to estimate the minimum elution volume of 5.5 M nitric acid required for complete recovery, we constructed elution histograms[7] by spiking high purity U_3O_8 samples with 5 mg each of Ti (IV) and V (IV) and collecting successive 20-mL fractions of elution solvent. Results are graphically depicted in Fig. 1. For Ti, a slightly higher volume for complete elution is observed, because the more unfavorable distribution coefficient for this element in the pure TBP-5.5 M nitric acid system.[10] An elution volume of 100 mL was considered reasonably safe for complete recovery (>95%) of both elements.

Flame Operating Conditions. It is well known[11] that elements like Ti and V which form stable monoxide molecules are better determined by atomic absorption with the use of a nitrous oxide-acetylene flame. The measured absorbance is critically dependent on flame composition.

Flame operating conditions were studied by the measurement of the absorbance for solutions of 5.5 M nitric acid containing, respectively, Ti 75 μg/mL and V 100 μg/mL, as function of the height above burner top. The

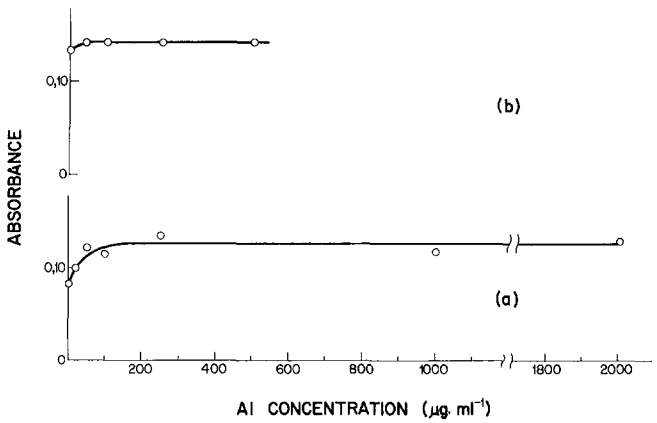

FIG. 2. Influence of aluminum on measured absorbance for (a) Titanium, (b) Vanadium. Solutions were 40 μg/mL of the tested element, 5.5 M nitric acid and 2000 μg/mL K.

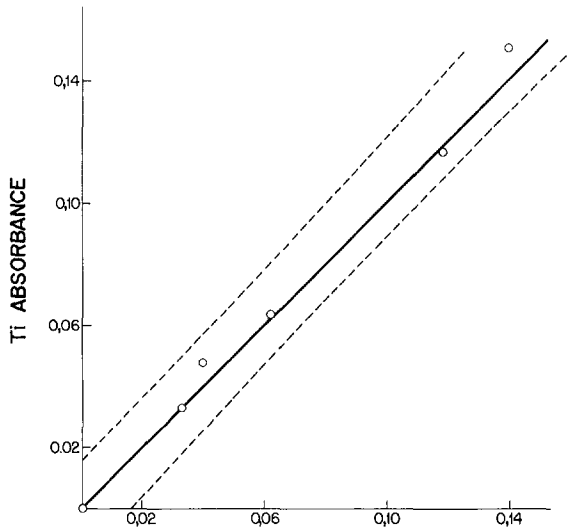

FIG. 3. Effect of V on Ti absorbance. Maximum V/Ti ratio tested = 10. Dotted lines are confidence hyperboles (5% probability level) for a straight line (not shown) fitted to experimental points.

spectrometer's conventional optics (nondiaphragmated light beam, focused near the center of the burner) was used without modification for these measurements. Oxidant (N_2O) flow rate was maintained at 7 L/min, and several acetylene flows were tested.

In both cases, near-stoichiometric flames (C_2H_2: 5.6 L/min for Ti and 5.2 L/min for V) produced the higher response, with a maximum at a height above the burner surface of about 5–6 mm for Ti and about 3–4 mm for V. These oxidant-to-fuel ratios were used for analytical work. The richer flame (C_2H_2: 6.0 L/min) produced a lower but more uniform absorbance through the whole interconal region (red feather) of the flame.

The existence of well-defined absorbance maximums in the flame employed suggested the possibility of increasing the Ti sensitivity by making the absorption measurements over a reduced flame area.[12] This effect has been observed for vanadium by Chakrabarti and McNeil.[13] The effect on the measured titanium signal produced by a 2-mm-wide light beam is shown in Table I for different analyte concentrations. A 40% increase in absorbance values is noted. It is worth mentioning that the signal-to-noise ratio was slightly degraded as a consequence of the higher phototube gain voltage required to compensate for the reduced monochromator acceptance angle.

Interference Studies. Ti and V are noticeably ionized in the nitrous oxide-acetylene flame.[11] Potential ionization interferences arising from the presence of alkaline and alkaline earth elements in yellow-cake samples were compensated for by the addition of 2000 μg/mL K (as potassium chloride) to sample and standard solutions.

Under the operating conditions examined, it was found that 5.5 M nitric acid solutions of Ti with 2000 μg/mL K added gave higher absorbances (about 20–40%) than aqueous solutions containing identical amounts of Ti and ionization supressor. The same effect was apparent for V, but to a lower extent. In order to verify if a change in the spatial distribution of analyte[14] in the presence of the mentioned concomitant can account for this observation, we prepared two solutions, one containing 200 μg/mL Ti and 2000 μg/mL K in 5.5 M nitric acid, and the other the same concentrations of Ti and K but in water. Using a 2-mm-wide light beam, we measured Ti absorbance for both solutions as a function of lateral translation in the flame at different heights. A definite enhancement of absorbance was observed with the nitric acid solution for the flame center but without a decrease in the outer portions. Consequently, it can be concluded that a lateral interference effect is not responsible for the enhancement. An increase in vaporization efficiency based on explosive fragmentation of partially desolvated droplets[15] seems a more plausible mechanism.

Table II shows the results of other interference stud-

TABLE II. Interferences on Ti and V: % variation of absorbance in presence of concomitant.

Titanium			Vanadium		
Analyte[a] concentration (μg/mL)	Concomitants and concentration level (μg/mL)	% Variation	Analyte[a] concentration (μg/mL)	Concomitants and concentration level (μg/mL)	% Variation
20	Fe 3000	+2.4	40	Fe 3000	−3.3
100	Fe 3000	−4.0	150	Fe 3000	−0.6
40	Al 1000	+54	40	Al 1000	+6.7
20	Fe 3000 + Al 1000	+57	40	Fe 3000 + Al 1000	+7.2
20	H_3PO_4 1800	+2.6	40	H_3PO_4 1800	+1.3
20	H_3PO_4 1800 + Al 1000	+52	40	H_3PO_4 1800 + Al 1000	+9.2

[a] Solution 5.5 M nitric acid, 2000 μg/mL K.

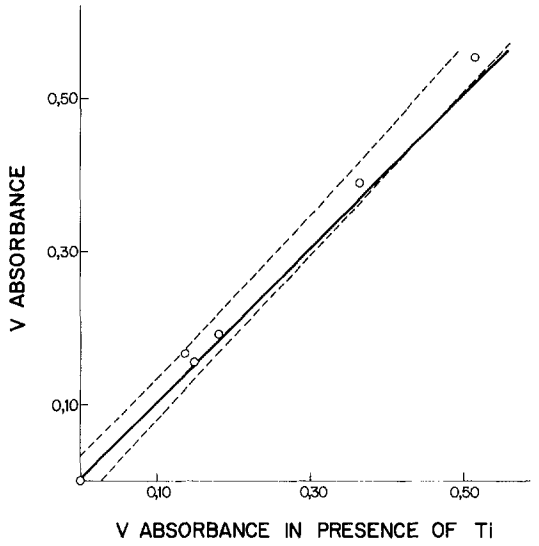

FIG. 4. Effect of Ti on V absorbance. Maximum Ti/V ratio tested = 5. Dotted lines are confidence hyperboles (5% probability level) for a straight line (not shown) fitted to experimental points.

ies in which Fe, Al, and P (added as phosphoric acid) were considered as concomitants.

Maximum concentrations tested correspond to expected values in real yellow-cake samples. Only solutions containing Al showed an appreciable (different from ±5%) variation of absorbance. The effect was more noticeable for Ti, as reported in the literature.[16]

Results of a more detailed study of this effect are shown in Fig. 2. Increased concentrations of Al were added to 5.5 M nitric acid and 2000 μg/mL K solutions containing, respectively, Ti and V 40 μg/mL, and absorbance was measured at the analytical wavelengths. The plots of absorbance vs. concentration of added Al leveled at about 200 μg/mL Al. Consequently, a concentration of 300 μg/mL in standard and sample solutions was considered sufficient to compensate for the presence of Al in analytical samples, with the additional advantage of an increased sensitivity for Ti. A possible explanation of the enhancement of the Ti signal in the presence of Al has been recently reported.[17]

Possible interferences due to background absorption in real sample 5.5 M nitric acid solutions containing Al and K were also investigated. Absorbance was measured at the V analytical wavelength with the use of a continuum source (hydrogen hollow-cathode lamp). In addition, two Ne lines at 363.37 and 369.42 nm generated by the Ti hollow-cathode lamp were employed for absorbance measurements at wavelengths near the Ti analytical wavelength. In both cases, background absorbance was found to be negligible.

Mutual interference effects between Ti and V have been reported in the literature.[16,18] The extent of this interference was verified for each element by the measurement of the absorbance of different sets of solutions with increasing concentrations of Ti (or V) in the presence and absence of varying amounts of V (or Ti). All solutions were 5.5 M nitric acid, 300 μg/mL Al, and 2000 μg/mL K. The concentration ratios Ti/V (or V/Ti) studied covered the range found when standard solutions

TABLE III. Recovery studies on synthetic samples.

Sample	% Titanium		% Vanadium	
	Added	Obtained	Added	Obtained
Nuclear grade U_3O_8	0.080	0.081	0.20	0.21
Yellow-cake A	0.042	0.039	0.086	0.086
% Fe: 4.9; % P: 0.9	0.46	0.45		
Yellow-cake B	0.036	0.035	0.072	0.074
% Fe: 2.6; % P: 0.9			0.64	0.71

containing both elements are employed for analytical calibration. For each element a plot of absorbance with no interferent added vs. absorbance when the possible interferent is added was obtained. The results are shown in Figs. 3 and 4. The straight line (slope = 1) represents a complete absence of mutually enhancing or depressing effects.

A further statistical analysis of these data was conducted. For each plot a straight line (not shown in the figures) was fitted to the experimental points by a least-squares procedure, and confidence hyperbolas at 5% probability level were calculated. These curves are shown as dotted lines on the plots of Figs. 3 and 4. No statistically significant difference between both theoretical and experimental curves could be detected for Ti in the presence of V. For V in the presence of Ti, the difference is slightly significant at the probability level tested, indicating a small depressive effect. This effect differs from that reported earlier in literature[18] and is presently being investigated.

Precision and Recovery Studies. Reproducibility for the complete analytical procedure was estimated with the use of real samples. For a concentration range of 0.1–0.2% of each element, the obtained relative standard deviation was 2.8% for Ti and 3.3% for V. Limits of detection, estimated from analytical curves, were 60 μg/g and 30 μg/g for Ti and V, respectively.

No standard reference material with certified concentrations of Ti and V was available. Recovery studies were performed on spiked high-purity U_3O_8 samples or synthetic samples prepared from uranium concentrates of known composition. The obtained results are given in Table III. Apart from an unexplained discrepancy for a rather high V concentration in sample B, a good agreement between added and obtained values is observed.

Because of the simplicity of the separation procedure, which requires little manipulation as compared with liquid-liquid extraction, the method can be easily adapted for routine controls in manufacturing plant laboratories. An additional advantage is that uranium can be determined on the same sample.

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Evaluation of Microwave-Induced Air-Plasma as an Excitation Source*

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A single-electrode atmospheric pressure microwave discharge air-plasma is reported. Fundamental characteristics, such as the effects of microwave power, auxiliary air flow, and nebulizer air flow on emission intensity, detection limits, and dynamic ranges for twelve elements and several interference experiments are reported. The plasma temperature is found to be about 4700°K. This simple system can be applied to the spectrochemical analysis of solution samples. The results with the use of this system to determine calcium, sodium, and potassium in SRM-1566 (oyster tissue) and SRM-92 (low-boron glass) show excellent agreement with the NBSs certified values.

Index Headings: **Emission spectroscopy.**

INTRODUCTION

Microwave-induced plasmas have long been used as excitation sources for spectrochemical analysis. Zander and Hieftje,[1] recently reviewed their principles, instrumentation, and uses. Most microwave plasmas are produced in a quartz tube located within a microwave supporting structure or within a resonant cavity which precludes operation at high power. Usually, only about 200 W or less power is required.

Recently, a single-electrode atmospheric pressure argon or helium microwave plasma has been described.[2] This plasma is easy to operate and can be used at fairly high power (about 500 to 600 W). Hanamura, Smith, and Winefordner[3] improved the single-electrode atmospheric pressure microwave plasma torch described by Yamamoto and Murayama.[4] This torch, which can be operated for a variety of gases, including Ar, He, and N_2, has a special platinum-clad electrode which minimizes wear of the plasma-support electrode, minimizes elemental contamination, and maximizes stability. This microwave plasma torch system has been used here with air as the plasma support gas and has been evaluated with respect to physical parameters, analytical figures of merit, and analytical uses.

EXPERIMENTAL

Apparatus. A block diagram of the microwave-induced air-plasma spectrometer system is given in Fig. 1. The instrumental components, including models and manufacturers are listed in Table I.

The microwave single-electrode plasma torch assembly is the same as the one described by Hanamura, Smith, and Winefordner.[3] The solution aerosol and the nebulizer gas are passed through from the bottom of the electrode into air plasma. The nebulizer system is shown in Fig. 2. With this system, when the nebulizer gas air flow is 2.2 L/min, the solution being aspirated is 1.2 mL/min and the aspiration efficiency is about 12%. The plasma observation zone is just above the top of the electrode. In this area, the signals obtained are high. However, the top of the electrode is bright when one is operating the plasma. In order to reduce the measured background emission, we used a 3-mm aperture in diameter in front of the monochromator slit.

Preparation of Standards. All stock solutions were prepared by dissolution of the standard materials in a certain amount of acid and were then diluted to the appropriate volume. All stock solutions were stored in polyethylene bottles which had been stored in nitric acid (1:4) for about 48 h and contained an acidity of 2% or 4%. All working solutions contained 1% HCl or HNO_3. The acid used was prepared by the use of a sub-boiling method. The reagents used are listed in Table II.

Preparation of the Oyster Tissue Solution. The preparation procedure is as follows: weigh 0.5 g of sample into a 250-mL Teflon® beaker; add several drops deionized water to wet it and then add 15 mL nitric acid (conc.); heat the solution with a lid to digest the sample. After the sample is decomposed, remove the lid and evaporate the solution to ~1–2 mL. Add several drops of perchloric acid (conc.) and heat to produce fumes until almost dry. After cooling, add 0.5 mL perchloric

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