Anal. Chem. 1994, *66*, 1540–1547

Determination of Chromium(VI) and Vanadium(V) Using an On-Line Anodic Stripping Voltammetry Flow Cell with Detection by Inductively Coupled Plasma Mass Spectrometry

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An on-line anodic stripping voltammetry (ASV) flow system, interfaced with an inductively coupled plasma mass spectrometric detector, was used to determine chromium(VI) and vanadium(V) and to eliminate polyatomic interferences which arise from sample matrices. The correct value was obtained for chromium in a certified water sample following oxidative pretreatment, using the conversion efficiency of Cr(III) to Cr(VI) as a correction factor. Cr(III) in diluted NIST SRM 2670 urine resisted oxidative conversion prior to analysis, although spikes of Cr(VI) were determined in this medium (recovery 62%). Results for vanadium in diluted SRM 2670 urine using the standard addition method were in good agreement with the quoted noncertified value. V(V) spike recoveries were 43% in urine and 67% in water. The matrix dependency of analyte recovery may be due to use of a carbon electrode in the ASV system. The elimination of polyatomic species ArC^+ and ClO^+ was quantitative for up to 10 000 μg/mL carbon and for 1000 μg/mL chloride. However, 10 000 μg/mL chloride was not quantitatively eliminated and yielded ClO^+ signals overlapping those of ^{53}Cr or ^{51}V, although ^{52}Cr was unaffected. The development of ASV protocols for both analytes using inductively coupled plasma atomic emission spectrometry detection is also discussed.

Chromium and vanadium are important target analytes in biological and environmental systems. Both of these toxic elements are used in the industrial sector, and there has been particular concern over workers' exposure to chromium(VI), which is now recognized as a probable agent of lung cancer in man[1,2] and which can produce gastrointestinal disorders, dermatitis, and ulceration of skin.[1] Chromium(VI) is also known to be present in certain water systems, due partly to industrial activity. Inductively coupled plasma mass spectrometry (ICP-MS) provides subnanogram per milliliter detection limits for both metals.[3] However, these analytes are subject to polyatomic interferences in ICP-MS which arise from very common sample matrix constituents: vanadium at $m/z = 51$ is overlapped by $^{35}ClO^+$ while chromium at $m/z = 52$ is overlapped by ArC^+.[3,4] In each case the overlapped analyte isotopes are by far the most abundant (^{51}V 99.76%, ^{52}Cr 83.76%), and use of alternate isotopes would give much poorer limits of detection.[5] Other interferences include $^{37}ClO^+$ on ^{53}Cr and $^{34}SO^+$ on ^{50}Cr.[4-6]

Chromium and vanadium may be deposited at a suitable working electrode and later released in anodic stripping voltammetry (ASV), while chloride and carbon-containing species generally do not deposit at the parameters required for analyte deposition. Therefore, ASV was investigated as a means of eliminating such concomitants in order to improve determination of chromium and vanadium in complex samples by ICP-MS. An efficient ASV flow cell, coupled with ICP-MS detection, had been demonstrated to accurately determine copper and cadmium in certified samples.[7] Concomitant elimination and signal enhancement by preconcentration were simultaneously and conveniently performed on-line, with the ICP-MS system completely isolated from the sample and supplied with a clean bypass solution (usually dilute HNO_3) until the analyte deposited at the electrode was released and directed to the ICP.[7,8] Although the ASV flow system could be used to obtain voltammetric data for electrochemically well-behaved analytes, the present emphasis is upon its use an an on-line method for improving spectrometric detection.

EXPERIMENTAL SECTION

Apparatus. Previous reports have described the design and construction of the ASV flow cell, based on a reticulated vitreous carbon working electrode, and the supporting manifold of valves and tubing.[7,8] All potentials are reported relative to Ag/AgCl. Inductively coupled plasma atomic emission spectrometry (ICP-AES) data were obtained using an ICP-2500 (Plasma-Therm, Kresson, NJ), and ICP-MS data using a VG PlasmaQuad (VG Elemental, Winsford, Cheshire, UK). Further information on these has been provided.[7,8] Parameters of operation for the ICP units are listed in Table 1.

Reagents. Distilled, deionized water (Barnstead, Boston, MA) was used for all solutions. The electrolyte system was

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0.1 M NH_4NO_3 (99.999%, No. 25,606-4, Aldrich, Milwaukee, WI) adjusted to pH 8.0 with concentrated NH_4OH (Fisher Scientific, Cincinnati, OH). The bypass solution directed to the ICP while ASV cell output was diverted to waste was 0.1 M HNO_3 (doubly distilled, No. 621, GFS Chemicals, Columbus, OH). Standards were prepared daily by serial dilution of 10 μg/mL stock solutions of ammonium vanadate-(V), vanadyl(IV) sulfate, chromium(III) nitrate, and potassium dichromate(VI) (ACS certified grade, Fisher). Urea and sodium chloride (Fisher) were used in the concomitant elimination experiments. Ammonium persulfate (Fisher) was used to oxidize Cr(III) to Cr(VI) as described below.

Procedure. Operation of the ASV flow system and the tubing manifold was as described previously,[7] except that the ASV cell supply electrolyte was continually degassed with helium but was used at room temperature. Samples were delivered to the cell at 1.0 mL/min, the flow rate for cell washout and analyte delivery to ICP was 1.70 mL/min, and sample volume was 1.0 mL at all times. A duration of 2 min/mL (which allowed for broadening of the sample plug during transport) was allowed for analyte deposition before the selection valve was switched to begin cell washout. Deposited analytes were stripped from the RVC electrode at 100 mV/s.

RESULTS AND DISCUSSION

Voltammetric Methods for Cr(VI). ASV has been infrequently used for determination of chromium(III),[9] but due to the greater hazard posed by chromium(VI), a method specific for the latter was desired. Chromium(VI) can be determined by ASV after deposition at a carbon electrode at pH values between 6 and 9 as follows:[9-11]

$$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^- \qquad E_0 = -0.13\ V$$

The chromate ion is reduced to Cr(III), which deposits at the electrode as a hydrous oxide of ill-defined stoichiometry, $Cr_2O_3 \cdot xH_2O$, more commonly designated as chromic hydroxide.[1,12]

Apparently only the CrO_4^{2-} ion participates. Below pH 1 the dominant species of Cr(VI) in solution is H_2CrO_4, between pH 2 and 6 $HCrO_4^-$ and $Cr_2O_7^{2-}$ exist in equilibrium, and CrO_4^{2-} is present at pH 6 and above.[1,13] The formation of $Cr(OH)_3$ is also enhanced at the pH required to maintain Cr(VI) primarily as CrO_4^{2-}.[1] However, freshly precipitated $Cr(OH)_3$ can dissolve in the presence of an excess of base,[1] making the ASV method most sensitive at pH between 7 and 9.[9] Cr(III) does not codeposit at the potential required for Cr(VI), providing state-specific detection. While chloride can deposit at mercury electrodes (as Hg_2Cl_2) at positive potentials,[9] making it a possible interferant in ASV analysis of Cr(VI) at Hg, this does not occur at carbon working electrodes.

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Table 1. Operating Conditions for ICP Instruments

ICP-AES	
radio frequency power	
forward	1.0 kW
reflected	<5 W
gas flows	
coolant	14.4 L/min
auxilliary	0.7 L/min
nebulizer	1.05 L/min
observed wavelengths	
chromium	267.716 nm
vanadium	309.311 nm
observation height	15 mm above load coil
monochromator slits	50 μm (entrance and exit)
ICP-MS	
radio frequency power	
forward	1.3 kW
reflected	<5 W
gas flows	
coolant	13.0 L/min
auxilliary	1.0 L/min
nebulizer	0.658 L/min
spray chamber	Scott-type double pass, cooled to 5 °C
sampling cone	nickel, 1.0-mm orifice
skimmer cone	nickel, 1.0-mm orifice
sampling distance	10 mm from load coil
pressures	
first stage	~1.5 mbar
second stage	$<1 \times 10^{-4}$ mbar
third stage	$\sim 2 \times 10^{-6}$ mbar
data acquisition	
single ion monitoring	
sweeps	1
dwell time	655, 360 μs
channels	4095
run time	2684 s
time-resolved acquisition	
dwell time	1280 μs
channels	512
mass range	50–54 *m/z* units

Preliminary Results in ASV-ICP-AES. (a) Cr(VI). In initial studies, ICP-AES was used to monitor the output of the ASV cell after the deposited analytes are stripped. Chromium(VI) required an electrolyte which was compatible with ICP nebulizer systems, but of suitable pH for the ASV process as described above. Previous work had shown that 0.1 mol/L NH_4NO_3 could be used with ICP-AES or ICP-MS without detrimental effects.[8] Adding ~300 μL of concentrated NH_4OH per liter gave a pH of 8.0. This solution proved compatible with ICP and was used as the sample electrolyte and the ASV cell supply electrolyte throughout the present work.

Figure 1 (upper display) shows voltammograms for both electrolyte blank and a sample containing 2 μg of Cr(VI), obtained using the aforementioned parameters for ASV flow system operation. This quantity of chromium is the largest that was examined in the course of the experiments. The stripping peak, reproducible in replicate runs, appeared as a broad curve with a maximum at ~+1.0 V. The known irreversibility of the electrochemical couple is probably partly responsible for the shape of the current signal. References for ASV of Cr(VI) on carbon at pH 8.0 quote the stripping potential as ~+0.6 V.[9]

Monitoring the ASV cell output in ICP-AES indicated that a final stripping potential of +1.3 V was required to completely release the chromium deposit from the electrode,

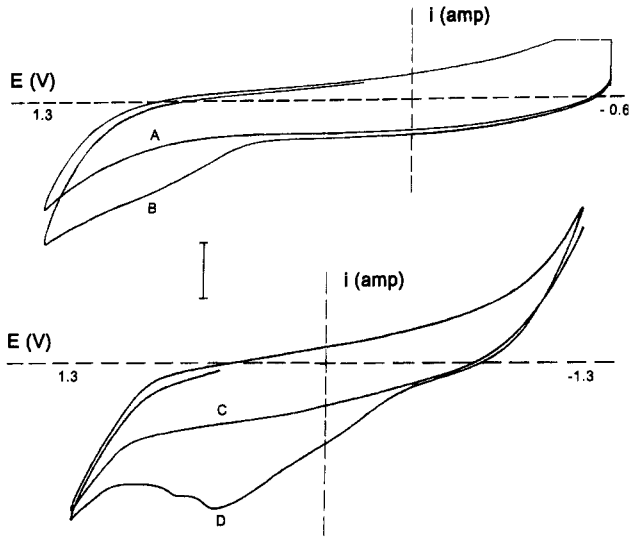

Figure 1. Voltammograms for analytes and blank (0.1 M NH_4NO_3 at pH 8.0), obtained using ASV parameters as described in text. Upper display: (A) blank; (B) 2 μg of Cr(VI). Lower display: (C) blank; (D) 30 μg of V(V). Vertical indicator mark equals 1 mA for upper display, 2 mA for lower display.

Table 2. Selected Results for Chromium(VI) and Vanadium(V) in ASV-ICP-AES[a]

	peak height	peak area
Chromium		
1 μg/mL Cr(VI) (successive days)	4.92 (5.3)	1.220 (3.5)
	3.10 (3.4)	1.034 (1.7)
	2.88 (6.8)	1.152 (1.2)
electrolyte blank	0.15 (31)	0.075 (4.2)
1.0 μg/mL Cr(III)	0.14 (6.3)	0.032 (37)
Vanadium		
500 ng/mL V(V)	1.87 (2.8)	3.26 (0.88)
500 ng/mL V(IV)	1.00 (3.6)	1.98 (3.05)
V(IV):V(V)	0.537	0.600

[a] RSD values (%) in parentheses ($3 < N < 5$). Abscissa has no units in ICP-AES signal display; units for peak heights and areas are arbitrary.

which may reflect slow dissolution of the gel-like chromium hydroxide.[14] This might in turn have influenced the peak profile observed in ICP-AES. After peaking, the chromium signal leveled to a plateau which then dropped gradually. This was not an artifact of the electrolyte since runs of the blank gave very low signals (Table 2), and tests demonstrated that switching the nebulizer feed from bypass solution to the ASV cell output did not by itself alter the ICP-AES signal. Figure 2 plots peak area observed by ICP-AES versus deposition potential for 1 μg/mL Cr(VI); –0.6 V gave the maximum response and was used for all remaining work with chromium.

Precision for 1.0 μg/mL Cr(VI) on three successive days is indicated in Table 2. Peak height RSD values were consistently higher than those for area, possibly due to the tailing of the peak signals. Mean peak heights on these days also varied to a greater extent than did peak areas. It was also confirmed that Cr(III) was unresponsive under the conditions used to deposit Cr(VI) at the electrode (Table 2).

(b) V(V). No literature concerning ASV of vanadium has been located to date by us. However, Cr(VI) and V(V) respond

(14) Hawley, G. G. *The Condensed Chemical Dictionary*, 9th ed.; Van Nostrand Reinhold Co.: New York, 1982.

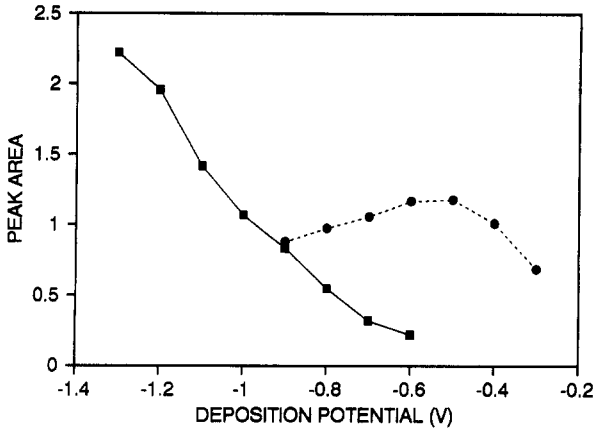

Figure 2. Deposition potential versus ICP-AES peak area for Cr(VI) and V(V). Samples: 1 μg/mL Cr(VI) or V(V) in electrolyte. Peak area units are arbitrary. Solid line, V(V); dashed line, Cr(VI).

in a similar manner in cathodic stripping voltammetry at a mercury electrode.[9,10,15] Since anodic stripping had worked for Cr(VI) at carbon, it was suspected that vanadium would also respond. Figure 1 (lower display) shows voltammograms for an electrolyte blank and a sample containing 30 μg of V(V), obtained by use of the aforementioned ASV system parameters. No more than 2 μg of V(V) was examined in the course of experiments using the ICP detector; however, such levels gave broad current responses, similar to those for Cr(VI) but of lower magnitude. To better characterize the behavior of the system, a higher level of V(V) had to be used. The current signals showed a broad peak at +0.55 V, with a shoulder at +0.75 V. The shape of these signals, which were reproducible in replicate runs, may reflect electrochemical irreversibility as well as ohmic potential drop due to the rather large stripping current flow.

A 1.0 μg/mL V(V) sample was prepared in 0.1 M NH_4NO_3 electrolyte adjusted to pH 8.0. Monitoring the ASV cell output using ICP-AES indicated that the potential required for efficient stripping was ~+1.0 V. Vanadium peak response in ICP-AES improved with increasingly negative deposition potential at least up to –1.3 V, showing no maximum as chromium had (Figure 2). A deposition potential of –1.3 V was used for all further work with V(V). It is not presently known whether V(V) deposits as the metal or another distinct species. The ICP-AES peak signals for vanadium exhibited some tailing but no plateau as the chromium peak signals had (it will be shown that this did not hold at the ICP-MS level). Precision was again superior for peak areas.

Since the oxidation state of vanadium in real samples would not be known with certainty, the response of states other than V(V) was investigated. Vanadium(IV) was considered most likely to appear as a competing species. The mean peak area signal for 500 ng/mL V(IV) deposited at –1.3 V was only 60% of that obtained for the same concentration of V(V) (Table 2), indicating that deposition was less efficient for the former.

Oxidative Conversion of Chromium(III). It was known that chromium in certified samples might be present in the trivalent state, and in order to compare experimental and certified values for total analyte, a reliable means of oxidizing chromium(III)

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to chromium(VI) would have to be applied prior to analysis by ASV-ICP. The intention was only to establish that a known level of chromium(VI) could be determined accurately by the method; such pretreatment would of course not be necessary or desired for specific detection of unknown levels of Cr(VI) in real samples.

Pretreatment methods were investigated for the oxidation of Cr(III), including alkaline permanganate[16] and acidic Ce(IV);[17] several of these proved unacceptable for various reasons. Ammonium persulfate[11,16] was the most suitable reagent among those tested. A 1 mL sample of 0.1 M $(NH_4)_2S_2O_8$ was added per 100 mL of a test sample (1 μg/mL Cr(III) in 0.1 M HNO_3). The mixture was boiled for 20 min, then cooled, and diluted to nearly the original volume. The mixture was made 0.1 M in NH_4NO_3, and concentrated NH_4OH was used to adjust pH to 8.0 before final dilution to 100 mL.

Chromium(VI) standards of 500 ng/mL and 2 μg/mL were used to generate a peak area calibration plot in ASV-ICP-AES; the data were corrected for electrolyte blank signal and zero was taken as a third point. The ICP-AES chromium signal peak produced by the persulfate reagent blank was equal to that of the electrolyte blank. The yield for the treated 1 μg/mL Cr(III) sample (0.698 μg/mL Cr(VI)) indicated that oxidative conversion efficiency was only 70%. The continuous nebulization signal for chromium in the treated sample (determined against the standards) was 1.05 μg/mL, proving that analyte had not been lost from the solution. Reasons for the nonquantitative conversion have not yet been determined. Despite this limitation, the persulfate treatment was the most efficient method for Cr(III) oxidation that had been tested at the time and ASV-ICP-MS experiments were done.

Determination of Cr(VI) and V(V) by ASV-ICP-MS. The ASV flow system was interfaced with ICP-MS for analysis of vanadium and chromium(VI) on two separate occasions, several months apart. Results for the first session of experiments have been detailed elsewhere;[18] results for the more extensive second session follow. The analytes were determined in two certified samples, Trace Metals–Water Supply, Lot WS378/6 (obtained from the U.S. Environmental Protection Agency), and National Institute of Standards and Technology SRM No. 2670 (Toxic Metals in Urine), which had been determined successfully in earlier ASV-ICP-MS studies.[7] The NIST set contains normal and elevated urine samples; only the latter was analyzed, partly because no value was quoted for vanadium in the former. Both samples had certified levels of total chromium, and a noncertified value was given for vanadium in the urine. Although the vanadium level of the water was not certified, spike recoveries of V(V) in water could be compared to those in dilute urine to illustrate dependence of analyte response on sample matrix.

The urine sample was treated with persulfate as described above following 10-fold dilution with water and was then made 0.1 M in NH_4NO_3 and adjusted to pH 8.0 with concentrated NH_4OH. As in earlier work,[7] the urine was diluted to minimze possible fouling of the electrode with organic sample constituents. The water sample was divided into two portions; one was pretreated to oxidize Cr(III) to Cr(VI), and the other was not pretreated and was analyzed for vanadium only. Both were made 0.1 M in NH_4NO_3 and pH adjusted. Since the ICP-AES results had indicated that persulfate oxidation of chromium was not quantitative, a synthetic sample of 40 ng/mL Cr(III) in water was treated and analyzed to allow calculation of conversion efficiency. Two spiked solutions were prepared for each sample to permit analysis by the method of standards addition and observation of spike recoveries.

Table 3. Calibration and Standard Addition Plot Parameters for Determination of Cr(VI) and V(V) by ASV-ICP-MS[a]

	slope (area cts mL/s ng)	intercept (area cts/s)	corr coeff
	Chromium(VI)		
calibration plot	29 231	−11 398	0.999 48
std addn urine	18 753	436	0.998 82
std addn water	31 901	679 074	0.999 56
	Vanadium(V)		
calibration plot	34 420	−9 520	0.999 76
std addn urine	13 428	203 617	0.999 99
std addn water	23 485	74 327	0.999 83

[a] Second session of experiments.

The analytes were detected in ASV cell output using single ion monitoring (Table 1). Calibration plots were generated with standards (in NH_4NO_3/NH_4OH electrolyte) ranging up to 50 ng/mL. Parameters of the calibration and standard addition plots are listed in Table 3. All results were corrected for the mean peak area of the electrolyte blank or the persulfate reagent blank, depending upon sample preparation.

Detection Limits. (a) Cr(VI). As in ASV-ICP-AES, chromium peak profiles observed in ASV-ICP-MS exhibited plateaus, the heights of which were proportional to Cr(VI) concentration (Figure 3). RSD values for the blank and calibration standards ranged from 1.1 to 5.7%. The method detection limit (three times the standard deviation of electrolyte blank peak area divided by plot slope) was 112 pg (or 112 pg/mL for a 1-mL sample), comparable to the continuous nebulization detection limit, 107 pg/mL (3σ of baseline signal).

(b) V(V). The signals observed in ICP-MS for vanadium exhibited the same kind of peak/plateau profile that had been observed for chromium, but the plateau height was the same for all standards and samples regardless of concentration (Figure 4) and was also observed for the electrolyte blank. The plateau portion of the signal was evidently too low to have been visible in ICP-AES.

The detection limit of vanadium in continuous nebulization, calculated as 3σ of baseline, was 57 pg/mL. The peak area RSD of the electrolyte blank in ASV-ICP-MS (8.7%) was high relative to those for calibration standards (1–3.5%). The method detection limit, calculated as for chromium, was 1.2 ng/mL. The imprecision of the blank signal was responsible for degrading the detection limit relative to that for continuous nebulization. (In the aforementioned first session of ASV-ICP-MS work, blank signal precision was superior[18] and the detection limit was 0.22 ng/mL.)

Results. (a) Chromium. In the first session of ASV-ICP-MS work, the chromium in NIST SRM 2670 Elevated Urine

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(18) Pretty, J. R. Ph.D. Dissertation, Department of Chemistry, University of Cincinnati, 1991.

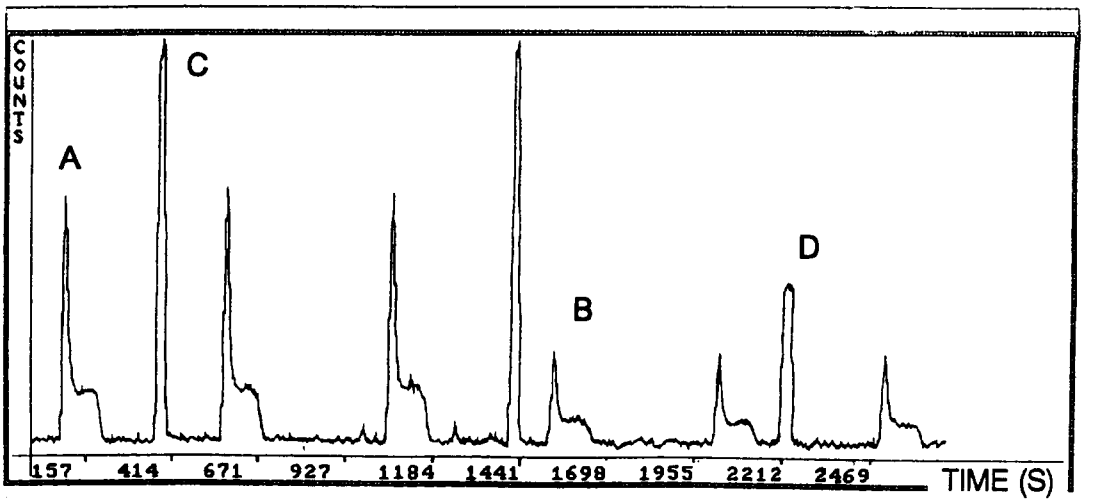

Figure 3. ICP-MS signals at $m/z = 52$. Peaks obtained with ASV flow system for (A) 25 and (B) 10 ng/mL standards of Cr(VI). Continuous nebulization signals for (C) 25 and (D) 10 ng/mL Cr(VI) are also shown.

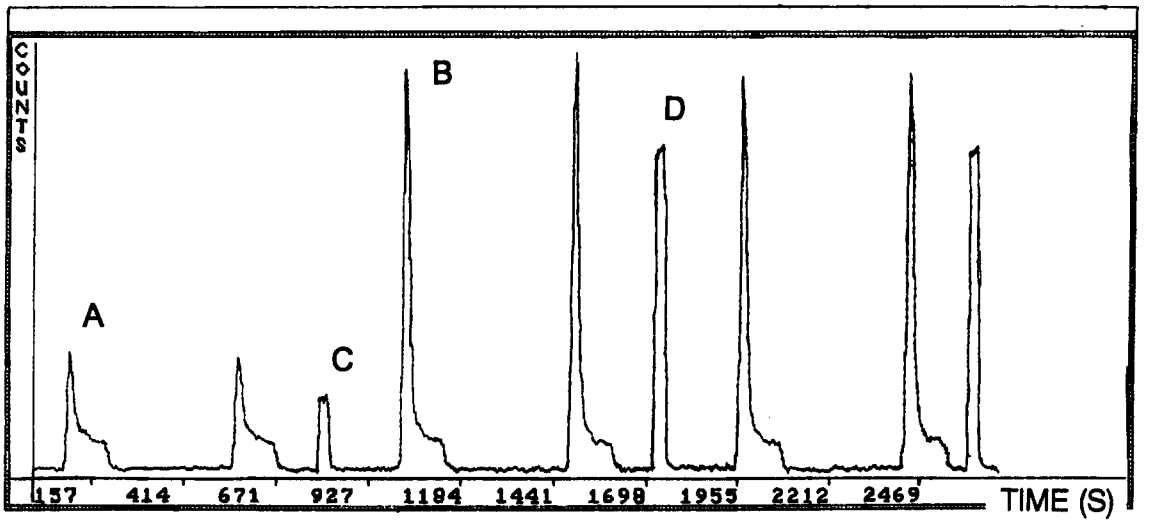

Figure 4. ICP-MS signals at $m/z = 51$. Peaks obtained with ASV flow system for (A) 1 and (B) 5 ng/mL V(V) standards. Continuous nebulization signals for (C) 1 and (D) 5 ng/mL V(V) are also shown.

had given no response (no oxidizing pretreatment was applied), suggesting that, as expected, the analyte was not present to any measurable extent as Cr(VI). However, the very low response obtained in the second session of experiments (Table 4) indicated that the persulfate treatment had been ineffective for oxidizing Cr(III) in dilute urine. Ammonium persulfate has been used to oxidize Cr(III) in seawater[16] and released the metal from colloids and highly stable complexes with organic ligands. Evidently Cr(III) in the urine matrix remained bound by a high proportion of organic constituents such as proteins, or possibly the level of persulfate used here was insufficient to both free the bound Cr(III) and oxidize it.

Recoveries of Cr(VI) spikes in 10-fold diluted NIST 2670 urine averaged 62% (Table 4), indicating that the ASV-ICP-MS system would respond to Cr(VI) in this matrix, although with reduced sensitivity relative to the calibration plot. (Spike recovery in the same matrix during the first session of ASV-ICP-MS work had averaged 57%.[18]) The lack of response of the unspiked sample thus does appear to have been due to a failure to convert the analyte to Cr(VI). The standards addition method might therefore allow the determination of unknown levels of Cr(VI) in dilute urine. The present standards addition results unfortunately do not demonstrate this conclusively, since the level of analyte in the urine which was present as Cr(VI) after treatment is not known with certainty.

Better results were obtained for the water sample (Table 4). The certified chromium level was 31.0 ng/mL. Untreated water gave 2.7 ng/mL Cr(VI), meaning that 28.3 ng/mL of the total chromium was probably present as Cr(III). Recovery of chromium(VI) for the treated synthetic sample of Cr(III) was 71.8% (Table 4), a conversion efficiency similar to that observed in ASV-ICP-AES. Based on this conversion efficiency, persulfate treatment of 28.3 ng/mL Cr(III) would yield 20.3 ng/mL Cr(VI). The total response for the treated water sample would then be the sum of original and newly converted Cr(VI), or 23.0 ng/mL. This is in excellent agreement with the value of 23.4 ng/mL Cr(VI) obtained for the treated water sample by calibration plot. A slightly lower value (21.3 ng/mL Cr(VI)) was obtained by standards addition. Cr(VI) spike recoveries were a little over 100%, with spike 1 within one standard deviation of quantitative recovery (Table 4). These results suggest that the ASV-ICP-MS method may prove suitable for direct determination of Cr(VI) in water. Had the conversion of Cr(III) to Cr(VI)

Table 4. Determination of Chromium(VI) by ASV-ICP-MS[a]

samples	true (ng/mL)	exp (ng/mL)	% rec
treated Cr(III)	40.0	28.7 ± 0.7	71.8 ± 1.8
water			
untreated	31.0 ± 4.9	2.7 ± 0.9	*b*
treated (calc plot)	31.0 ± 4.9	23.4 ± 0.7	75.5 ± 2.3
treated (std addn)	31.0 ± 4.9	21.3 ± 1.6	68.7 ± 5.2
treated spiked soln 1	41.0 ± 4.9	33.8 ± 0.8	82.4 ± 2.0
spike 1 only	10.0	10.4 ± 1.0	104 ± 10
treated spiked soln 2	51.0 ± 4.9	45.2 ± 0.9	88.6 ± 1.8
spike 2 only	20.0	21.8 ± 1.2	109 ± 6.0
urine			
elevated (calc plot)	8.5 ± 0.6	0.2 ± 0.8	*b*
elevated (std addn)	8.5 ± 0.6	0.4 ± 0.6	*b*
elevated spiked soln 1	18.5 ± 0.6	6.1 ± 0.8	*b*
spike 1 only	10.0	5.9 ± 1.1	59.0 ± 11
elevated spiked soln 2	28.5 ± 0.6	13.0 ± 0.7	*b*
spike 2 only	20.0	12.8 ± 1.1	64.0 ± 5.5

[a] All urine samples treated with persulfate. Water samples treated except as indicated. $N = 3$ for all. Experimental values reported to ±1 standard deviation. [b] Most Cr in sample was in unresponsive state and recovery is not listed.

Table 5. Determination of Vanadium by ASV-ICP-MS[a]

samples	true (ng/mL)	exp (ng/mL)	% rec
urine			
elevated (calc plot)	12	6.2 ± 0.5	51.3 ± 4.2
elevated (std addn)	12	14.2 ± 0.02	118 ± 0.2
elevated spiked soln 1	22	10.5 ± 0.5	47.7 ± 2.2
spike 1 only	10.0	4.3 ± 0.7	43.3 ± 7.1
elevated spiked soln 2	32	14.8 ± 0.5	46.3 ± 1.5
spike 2 only	20.0	8.7 ± 0.7	43.5 ± 3.5
water			
(calc plot)	unkn	2.5 ± 0.5	unkn
(std addn)	unkn	3.2 ± 0.3	unkn
spiked soln 1	unkn	9.1 ± 0.5	unkn
spike 1 only	10.0	6.6 ± 0.7	66.1 ± 7.1
spiked soln 2 ($N = 2$)	unkn	16.2 ± 0.5	unkn
spike 2 only	20.0	13.6 ± 0.7	68.0 ± 3.7

[a] Persulfate treatment applied to diluted urine samples only. $N = 3$ for all samples except as indicated. Experimental values reported to ±1 standard deviation. No vanadium certification quoted for water sample; the vanadium level quoted for NIST SRM 2670 Elevated Urine is noncertified.

been quantitative, the analysis of the water sample would then have yielded the certified value of 31.0 ng/mL total chromium. Such pretreatment would obviously be unnecessary for determining the Cr(VI) content of unknown water samples.

(b) Vanadium. Results for 10-fold diluted NIST SRM 2670 urine are listed in Table 5. By the calibration plot, recovery for vanadium in unspiked urine was 51%, and V(V) spike recoveries averaged only 43%. However, the standards addition method gave 14.2 ng/mL vanadium, comparable to the quoted noncertified value of 12 ng/mL after dilution. (In the first ASV-ICP-MS session, the standards addition method gave 12.8 ng/mL vanadium.[18])

Results for the water sample (Table 5) indicate that, as for Cr(VI), analyte response was superior to that obtained in diluted urine. Recovery for the unspiked sample cannot be determined without analyte certification, but V(V) spike recoveries averaged 67%. The linear standards addition plot gave a slightly higher value for vanadium in unspiked water than did the calibration plot (Table 5). Results for both urine and water samples indicate that the standards addition method is necessary to determine vanadium by ASV-ICP-MS with the present system. Due to the lower slopes of the standards addition plots (relative to that of the calibration plot), sensitivity would be compromised for the present sample matrices.

The variation in analyte recoveries may be due to the use of an unmodified carbon working electrode. Organic constituents such as proteins are present in the urine sample, and such species would be expected to have an affinity for adsorption at carbon. This could result in partial blockage of the active electrode surface area, diminishing analyte deposition efficiency in urine relative to that observed for standards prepared in pure electrolyte media. Without rigorous conditioning in the course of analysis, the electrode might retain such adsorbents even after exposure to the offending matrix has ceased. In this context, it may be noted that the approximately quantitative recoveries for Cr(VI) described above were obtained prior to the analysis of dilute urine. However, the analysis of V(V) in water, for which analyte spike recoveries were nonquantitative, was performed following determination of both analytes in the urine sample. Reduced response was not observed when copper and cadmium were determined in NIST SRM 2670 urine by ASV-ICP-MS using mercury-coated carbon electrodes.[7] Mercury would have lower affinity for organic species than bare carbon and would be less likely to be fouled by adsorption. It is also known that mercury deposits on carbon substrates as droplets rather than an unbroken film, and preferential organic adsorption at the remaining carbon sites might further discourage fouling of the mercury.

Elimination of ArC^+ and ClO^+ Interferences in ICP-MS. The ability of the ASV flow system to eliminate polyatomic ion interferences due to chloride and carbon concomitants was examined using a format which had worked well in removing $ArNa^+$ due to high levels of sodium.[7,18] After each sample injection had cleared the flow system, the ASV cell was flushed with clean supporting electrolyte at 1.70 mL/min for 4 min. Time-resolved acquisition (TRA) software was used to obtain simultaneous readings at m/z values of 50–54 (Table 1). Because TRA is less sensitive than single ion monitoring, relatively high levels of analyte (25 ng/mL V(V), 50 ng/mL Cr(VI)) were used. Concomitant levels were 1000 and 10 000 μg/mL. Carbon was added as urea and chloride as NaCl; these reagents did not greatly affect sample pH, and only small amounts of concentrated HNO_3 or NH_4OH were required for adjustment.

Tables 6–8 list peak area counts for electrolyte blank, concomitants, and analytes with and without concomitants, along with corrected counts for the analyte samples (the area count for blank or concomitant has been subtracted). Tables 6 and 7 show different peak area count values for 50 ng/mL Cr(VI) and the electrolyte blank; the data for chromium in carbon and in chloride were obtained months apart, and instrumental performance differed on each occasion. All chloride elimination data were obtained in the same session, hence the duplication of blank and concomitant values in Tables 7 and 8.

Elimination of ArC^+. Table 6 indicates efficient elimination of ArC^+ for determination of Cr(VI) in carbon. Comparing counts at $m/z = 52$ for electrolyte blank and concomitants suggests a trend toward higher signal, but the differences

Table 6. Mean Peak Area Counts for Chromium(VI) in Carbon Concomitant Elimination[a]

sample	net peak area counts $m/z = 52$	net peak area counts $m/z = 53$	^{52}Cr:^{53}Cr isotope ratios exp	exp/true (%)
electrolyte	5965 (2.7)	2255 (7.6)		
1000 μg/mL C	6442 (24)	1902 (5.9)		
10000 μg/mL C	7689 (13)	2239 (3.2)		
50 ng/mL Cr	55202 (3.8)	7925 (3.4)		
corrected	49237 (4.9)	5670 (5.6)	8.68	98.6
50 ng/mL Cr in 1000 μg/mL C	59003 (0.9)	7618 (2.8)		
corrected	52561 (3.1)	5716 (4.2)	9.20	104.5
50 ng/mL Cr in 10000 μg/mL C	57233 (2.0)	7985 (2.8)		
corrected	49534 (4.4)	5746 (5.2)	8.62	97.9

[a] RSD values (%) in parentheses. $N = 3$ for all samples. True abundance ratio of chromium isotopes is 8.86.

Table 7. Mean Peak Area Counts for Cr(VI) in Chloride Concomitant Elimination[a]

sample	net peak area counts $m/z = 51$	net peak area counts $m/z = 52$	net peak area counts $m/z = 53$	^{52}Cr:^{53}Cr ratios exp	exp/true (%)
electrolyte	6673 (7.0)	12223 (2.7)	3118 (5.8)		
1000 μg/mL Cl^-	6654 (4.9)	11648 (15)	3181 (4.7)		
10000 μg/mL Cl^-	14311 (8.3)	12803 (6.2)	5625 (5.1)		
50 ng/mL Cr ($N = 4$)	6509 (12)	47512 (3.7)	7209 (2.4)		
corrected	−164 (>100)	35289 (5.0)	4089 (6.1)	8.63	98.0
50 ng/mL Cr in 1000 μg/mL Cl^-	6184 (0.7)	46471 (1.7)	7105 (2.9)		
corrected	−470 (70)	34824 (5.4)	3924 (6.4)	8.87	100.7
50 ng/mL Cr in 10 000 μg/mL Cl^-	18263 (8.1)	46243 (2.3)	11001 (5.3)		
corrected	3952 (48)	33440 (4.0)	5376 (12)	6.22	70.6

[a] RSD values (%) in parentheses. $N = 3$ for all samples except as indicated. True abundance ratio of chromium isotopes is 8.86.

between these readings may be shown to be nonsignificant ($t < t_c$). Uncorrected counts do show a significant rise for Cr(VI) in 1000 μg/mL carbon relative to Cr(VI) alone. This was probably a random occurrence, since the value for Cr(VI) in 10 000 μg/mL carbon was not significantly greater ($t = 1.56$, $t_c = 2.78$) than that for Cr(VI) alone. Changes in count totals at $m/z = 53$ also showed no trend with concomitant level and were not significant in magnitude. Corrected counts show that analyte deposition efficiency was affected little by the concomitant; both values for Cr(VI) in carbon agreed acceptably with that for Cr(VI) alone ($t < t_c$). The true abundance ratio for ^{52}Cr:^{53}Cr is 8.86,[5] and the corrected count ratios matched this value well regardless of carbon level. Experimental ratio/true ratio was within a few percent of 100% in all cases (Table 6). Figure 5 shows TRA ion signals at $m/z = 52$ for electrolyte blank, 10 000 μg/mL carbon, and 50 ng/mL Cr(VI) alone.

Table 8. Mean Peak Area Counts for V(V) in Chloride Concomitant Elimination[a]

sample	net peak area counts $m/z = 51$	net peak area counts $m/z = 53$
electrolyte	6673 (7.0)	3118 (5.8)
1000 μg/mL Cl^-	6654 (4.9)	3181 (4.7)
10000 μg/mL Cl^-	14311 (8.3)	5625 (5.1)
25 ng/mL V	23377 (1.5)	2712 (3.2)
corrected	16704 (3.5)	−406 (49)
25 ng/mL V in 1000 μg/mL Cl^-	24248 (5.0)	2785 (0.9)
corrected	17594 (7.2)	−396 (38)
25 ng/mL V in 10000 μg/mL Cl^- ($N = 4$)	35978 (4.9)	6427 (6.7)
corrected	21667 (9.9)	802 (64)

[a] RSD values (%) in parentheses. $N = 3$ for all samples except as indicated.

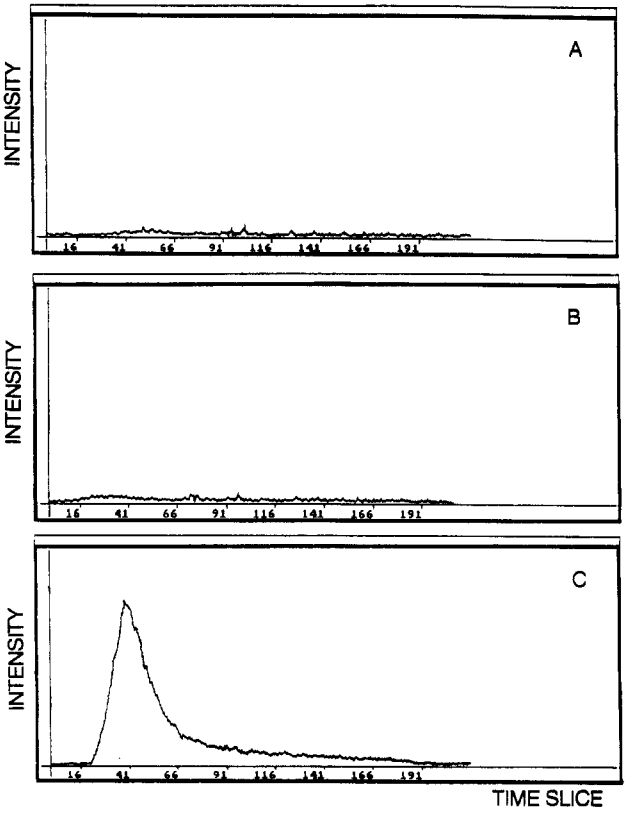

Figure 5. ICP-MS signal at $m/z = 52$ during release of ASV cell contents to plasma, demonstrating elimination of ArC^+ signal due to carbon concomitant. Samples are (A) electrolyte blank, (B) 10 000 μg/mL carbon in electrolyte, and (C) 50 ng/mL Cr(VI) in electrolyte. Scale is same for all. Obtained using TRA software; one time slice unit equals 0.75 s.

Elimination of ClO^+. Table 7 shows elimination of ClO^+ signals for determination of Cr(VI) in chloride. Corrected and uncorrected counts both indicate that 1000 μg/mL Cl^- did not significantly alter Cr(VI) signals at either $m/z = 52$ or 53 ($t < t_c$ when compared with counts for Cr(VI) alone). For Cr(VI) with and without 1000 μg/mL Cl^-, the ratio of corrected counts at $m/z = 52$ and 53 agreed well with the expected value of 8.86.

Corrected and uncorrected counts for Cr(VI) in 10 000 μg/mL Cl^- also agreed with those for Cr(VI) alone at m/z = 52 ($t < t_c$), indicating that the concomitant did not affect analyte deposition at the ASV cell electrode. However, uncorrected counts at m/z = 51 and 53 both increased (relative to the counts for chloride-free samples) in a ratio of ~3:1, evidence for chloride-based polyatomic ion interference (ClO^+). The signal change was larger for Cr(VI) in 10 000 μg/mL Cl^- versus Cr(VI) alone than it was for 10 000 μg/mL Cl^- versus the electrolyte blank; as a result, the corrected count for Cr(VI) at m/z = 53 is larger than expected, and the isotope ratio is incorrect (Table 7). This may indicate that the efficiency of elimination of 10 000 μg/mL Cl^- from the ASV cell varied over time (since the deposition of chromium was not significantly altered, the increase could not be due to ^{53}Cr). Since the ^{52}Cr isotope signal was not affected, Cr(VI) could still be quantified accurately in 10 000 μg/mL Cl^-, although the elevated counts at m/z = 53 would prevent positive identification of the element using isotope ratio determination.

Table 8 shows elimination of ClO^+ signals for determination of vanadium in chloride. The pattern was similar to that for Cr(VI) in the same system. At m/z = 51, corrected and uncorrected counts for V(V) in 1000 μg/mL Cl^- showed slight, nonsignificant enhancements relative to V(V) alone ($t < t_c$). Counts at m/z = 53 showed no significant change. Again, counts at m/z = 51 and 53 both increased sharply, in a ratio of roughly 3:1, for samples containing 10 000 μg/mL Cl^-. Corrected counts for V(V) at m/z = 51 were significantly higher than those for V(V) alone or in 1000 μg/mL Cl^-. This is certainly due largely to incomplete correction for ClO^+, since counts at m/z = 53 also increased. However, since vanadium is nearly monoisotopic, comparison cannot be made to an analyte signal elsewhere on the mass spectrum to demonstrate that the ASV deposition efficiency of the analyte had definitely not been altered by the presence of 10 000 μg/mL Cl^-.

For V(V) in 10 000 μg/mL Cl^-, the increase at m/z = 51 due to ClO^+ was 54% by uncorrected counts and 30% by corrected counts (Table 8). Compared with mean counts for chloride-free 25 ng/mL V(V), these increases are equivalent to, respectively, 13.5 and 7.5 ng/mL vanadium, or apparent total analyte levels of 38.5 and 32.5 ng/mL versus the true total of 25 ng/mL V(V). While this is a great improvement over the level of interference expected in the absence of concomitant elimination (see below), increases of this magnitude would be unacceptable for many determinations of vanadium at the ICP-MS level. Figure 6 compares TRA ion signals for the electrolyte blank, both chloride solutions, and 25 ng/mL V(V) alone, showing the small rise in signal produced by 10 000 μg/mL Cl^- and the size of this increase relative to the analyte peak.

Work involving the elimination of $ArNa^+$ to improve ICP-MS detection of copper had shown that 10 000 μg/mL sodium could be completely cleared from the ASV cell in 4 min.[7] However, a different supporting electrolyte (0.1 mol/L HNO_3) was used in those studies. It has been estimated that 500 μg/mL carbon and chloride would yield signals equivalent to 330 ng/mL vanadium at m/z = 51 and 60 and 1100 ng/mL chromium at m/z = 52 and 53, respectively.[4] This suggests

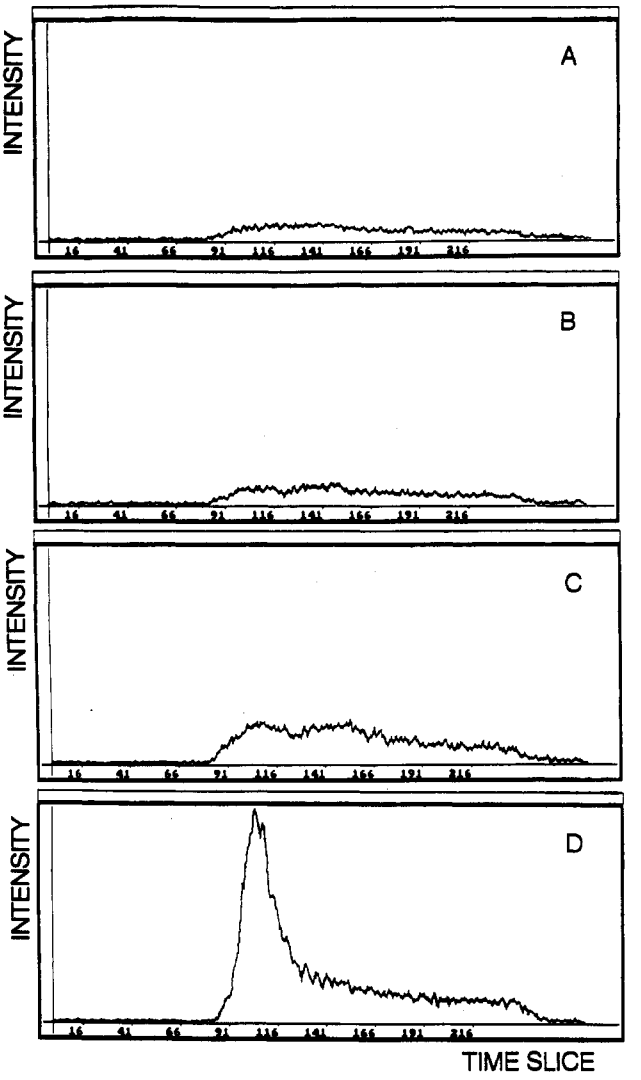

Figure 6. ICP-MS signal at m/z = 51 during release of ASV cell contents to plasma, demonstrating degrees of elimination of ClO^+ signal due to chloride concomitants. Samples are (A) electrolyte blank, (B) 1000 μg/mL Cl^- in electrolyte, (C) 10 000 μg/mL Cl^- in electrolyte, and (D) 25 ng/mL V(V) in electrolyte. Scale is same for all displays. Obtained using TRA software; one time slice unit equals 0.75 s.

the degree of interference which might be expected from 10 000 μg/mL of these concomitants if they are not eliminated (in fact, most ICP-MS sample introduction systems will not tolerate such high levels of dissolved solid).

ACKNOWLEDGMENT

Our gratitude to William Brauntz, Arthur Case, and Douglas Hurd of the Department of Chemistry Machine Shop for fabricating the components of the ASV flow cell, Robert Voorheis and Paul MacKensie of the Electronics Shop for technical assistance, and Douglas Heitkemper of U.S. FDA Forensics Center for obtaining the EPA water sample and certification data. The contents of this paper were presented in part at the 1990 FACSS Conference, Cleveland, OH, October 1990.

Received for review October 25, 1993. Accepted February 9, 1994.®

®Abstract published in *Advance ACS Abstracts,* March 15, 1994.