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HYDRIDE PRECONCENTRATION FOR INDUCTIVELY COUPLED PLASMA OPTICA--ETC(U)

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HYDRIDE PRECONCENTRATION FOR INDUCTIVELY COUPLED
PLASMA OPTICAL EMISSION SPECTROMETRY

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HYDRIDE PRECONCENTRATION FOR INDUCTIVELY COUPLED
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ABSTRACT

Studies are presented describing an improved application of the NaBH_4 reduction of soluble arsenite to form arsine as a preconcentration approach for ultra-trace level arsenic determination by inductively coupled plasma optical emission spectrometry (ICP-OES). Specialized analyte introduction techniques are described for elimination of reaction by-products that would normally extinguish a medium power plasma discharge. An approach is presented to minimize the need for background correction and facilitate a superior arsenic detection limit (≤ 0.03 ng/mL) in a relatively inexpensive 1.2 kW ICP system.

INDEX HEADINGS: Emission spectroscopy; Inductively coupled plasma;
Hydride preconcentration; Arsenic, Trace analysis.

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INTRODUCTION

The excellent detection limits of inductively coupled plasma optical emission spectrometry (ICP-OES) for many elements (1) in conjunction with the inherent simultaneous multielemental detection possibilities offered by emission spectroscopy have made the ICP a powerful new method for determination of trace elements in environmental materials. Despite the general desirability of ICP spectrometry, some toxic non-metals are unfortunately present in environmental samples at levels too low to detect by either ICP-OES or atomic absorption when nebulizer sampled introduction is employed. Olson, Haas, and Fassel recently reported a detection limit of 2 ng/mL arsenic on a 2σ signal basis using a flow-through approach to ultrasonic nebulation with the ICP (1). The authors stated that a more conservative 3σ value (3 ng/mL) would be more valid (1). Since reliable quantitation (better than 5% RSD) is only achieved for concentrations greater than \sim five times the limit of detection (2), the ICP method of Olson, Haas, and Fassel (1) appears to provide quantitative precision for arsenic determination only above levels of \sim 15 ng/mL. Although this technique represents a valuable development in emission spectroscopy and provides a far lower arsenic detection limit than nebulizer-flame approaches, it remains less than adequate for reliable quantitative measurement of the levels of arsenic (< 10 ng/mL) occurring in many environmental materials such as natural water samples (3). Direct sample introduction methods (e.g., nebulizer) for the ICP have also been shown to lead to severe interference by background spectra (stray light, etc.) resulting from excessively intense emission of species such as calcium present in complex samples (4). A variety of schemes for background elimination or correction involving interference filters, solar blind photomultiplier tubes, double monochromators, and/or wavelength modulation have been utilized to alleviate

the problem (4). A more sensitive approach of reduced susceptibility to spectral interference is clearly desirable.

Hydride generation is commonly employed in atomic absorption spectrometry as a preconcentration method to improve the detection limit of arsenic determination (5). This relatively inexpensive alternative to flameless atomization of arsenic for AA involves near quantitative conversion of the oxidized forms of arsenic in a 25-100 mL sample volume to form arsine. This volatile product flows to the burner as a discrete "plug" of analyte, thus effecting a net preconcentration that dramatically improves the concentration detection limit when compared to nebulizer introduction of the sample. Hydride preconcentrations have been used in a variety of instrumental methods (5-61). Although possible chemical solution interferences with the hydride reduction are under investigation (25, 35, 38, 52, 54, and 61), a further advantage appears to include resultant separation of arsenic from the sample matrix, thereby excluding many species (e.g. calcium) that might otherwise cause spectral interferences. The qualities associated with hydride generation techniques are desirable for emission spectroscopy as well as AA and have, therefore, resulted in application of this approach to d.c. and microwave discharges (12,47) as well as the preparation of electrodeless discharge lamps (62). An inherent problem with the hydride generation that has delayed successful application of this method to the ICP is that of chemical reaction by-products (H_2 , H_2O , and CO_2) that can extinguish a medium or low power plasma when introduced along with arsine.

To our knowledge, the only successful literature report of hydride preconcentration applied to the inductively coupled plasma is the recent effort of Thompson, Kirkbright, et. al. (60, 61). In order to keep the plasma from extinguishing, relatively high rf power levels (2.7 kW - 5.0 kW)

were employed (60). Several further steps were also necessary to stabilize and limit the flow rate of H_2 - a reaction by-product (60). First, the sample and reagent volumes were continuously mixed. The instantaneous mixed volume was relatively small compared to that of earlier atomic absorption work. This would result in a smaller flow rate of undesirable H_2 produced. Unfortunately, it also would lead to lesser instantaneous amounts of AsH_3 produced and delivered to the plasma. Second, the concentration of $NaBH_4$ reagent was reduced to 1% (60). This would decrease the amount and rate of H_2 evolution. Thompson, Kirkbright, et. al. state that stable plasmas could not be maintained if the reagent concentration exceeds 1.5% $NaBH_4$ (60). Third, Thompson, Kirkbright, et. al. state that any pulsation in the reagent delivery pump leads to corresponding irregularities in the undesirable H_2 evolution (60). According to the authors, this produced marked fluctuations in the character of the plasma (60). It should be apparent from the experience of Thompson, Kirkbright, et. al. (60, 61) that the ICP does not tolerate the H_2 by-product very well. Much compromise was necessary to reduce and stabilize the rate of H_2 evolution in order to avoid extinguishing even the high powered (2.7 kW - 5.0 kW) plasma. It is not surprising then, that the ICP limit of arsenic detection achieved for hydride preconcentration by Thompson, Kirkbright, et. al. was 0.8 ng/mL (60). This value is only slightly better than the 2 ng/mL reported for ICP by Olson, Haas, and Fassel (1) using ultrasonic nebulizer introduction of sample.

The purpose of the present work is to present separation and low temperature entrapment techniques that exclude undesirable reaction by-products (e.g. H_2) and result in a superior concentration detection limit in the ICP determination of arsenic via the generation of its volatile hydride. Resultant separation of analyte from the matrix and the by-products permits use of a much lower power plasma (1.2 kW input power) and a small

monochromator (0.35 meter) since the spectrum is no longer complex in the absence of matrix species. Experimental conditions are outlined to minimize the need for elaborate background processing and correction schemes.

I. EXPERIMENTAL

A. Apparatus. The plasma system and spectrometer are described in Table I. The hydride generation and sample introduction apparatus are diagrammed in Fig. 1. Symbols V_1 , V_3 , and V_4 represent Teflon stopcocks. V_2 was a ground glass stopcock. V_5 was a needle valve. The reagent syringe utilized was the standard ground glass type. A 6 mm x 16 mm "football" - shaped Teflon coated stirring bar was used. The reaction vessel was designed to hold up to 25 mL of sample. The capacity can easily be increased to 100 mL by using a larger vessel and an appropriately extended bubbler. NaBH_4 was added through a capillary tip drawn from 2 mm Pyrex tubing.

B. Reagents. 5% NaBH_4 in dilute NaOH was prepared from Alfa Inorganics (Danvers, Mass.) 89% pelletized NaBH_4 or the 99% analytical grade NaBH_4 powder. "Suprapur" (E & M Laboratories, Darmstadt, West Germany) or A.R. grade hydrochloric acid was diluted to ~ 1 N as the working level in all samples. The As (III) standard was prepared (64) at the 1 ppm level from which 5-200 μL aliquots were taken for addition to the sample. Indicating "Drierite" (Xenia, Ohio) was used as a drying agent to prevent ice buildup in the cold trap and/or water vapor from extinguishing the plasma. Dry NaOH pellets (A.R. grade) were employed to remove CO_2 from the system. Liquid argon used to cool a 26 cm total length of 3.17 mm o.d. stainless steel tubing employed as a "U" trap is commercially available. Argon may alternatively be liquefied in the laboratory by flowing gaseous argon at 12 L/min through 3 turns (25 mm radius) of 6.35 mm o.d. copper tubing submerged in liquid nitrogen. Longer coils may not be submerged or the argon will solidify, but parallel multiple submerged coils may be employed. This

flow rate and coil configuration is sufficient to produce ~ 400 mL per hour (per submerged coil) of liquid argon streaming from the end of the coil into a second collection dewar.

C. Procedure. The analytically observed zone was centered 1 cm above the r.f. coil. Horizontal position was optimized by moving the plasma while monitoring a carbon line (247.856 nm) emitted continuously by plasma gas impurities. Atomic arsenic lines were isolated initially while monitoring the emission spectrum of a temporarily mounted arsenic hollow cathode lamp. The hollow cathode lamp was then turned off.

The following procedural steps were evolved for determination of arsenic in natural water samples:

The system is turned on allowing the water bath to equilibrate at approximately 60°C. The 193.696 nm line is isolated using a 25-50 μ m slit. Valve V_1 is closed, V_4 opened, and V_2 , V_3 , and V_5 are turned to flow argon through all torch lines for several minutes (see Fig. 1). V_3 is closed and the plasma ignited. No "sample gas" is used at this point. A 25 mL sample and 2.5 mL of conc. HCl are pipetted into the clean reaction vessel through the sidearm. The vessel is then stoppered tightly. Valve V_3 is turned to bypass the plasma with the "sample gas" stream. Valve V_2 is turned to permit eventual reaction products to later enter the cold trap. Valve V_4 is closed, the stirring bar activated, and argon (~ 1.5 L/min) is bubbled through the sample for 30 sec. The cold trap is immersed in liquid argon so that a section of tubing about 26 cm in length is cooled. Approximately 15 sec are allowed for equilibration. Valve V_1 is turned, and 2.5 mL BH_4^- reagent is drawn into the syringe (see Fig. 1). Valve V_1 is turned in the opposite direction and the reagent is added to the sample in a steady dropwise fashion over a period of one minute. Valve V_2 is closed and valve V_4 opened before pressure builds up. Valve V_2 is turned to select the auxiliary argon line ("sample gas"), thereby excluding the reaction vessel. After 5 sec, the "sample gas" is turned off by closing V_5 which is a needle valve. Valve V_3 is turned to expose the plasma to the eventual cold trap effluent. The "sample gas" is slowly turned on using the

V₅ needle valve in order to establish the central low pressure channel in the plasma discharge (final flow rate 0.9 L/min with valve wide open). The chart recorder is activated (full scale equivalent 10^{-8} amp). The liquid argon dewar is removed, a 3 sec pause is observed, and the cold trap is quickly immersed in lukewarm water. The transient arsenic signal appears at the recorder completely time resolved from any significant background signal variation. Valve V₃ is closed, the cell is emptied and rinsed through the sidearm using the probe attached to the water aspirator, and all steps are repeated for subsequent samples, standard "adds", and reagent blanks.

This procedure results in conversion of arsenate and arsenite (50) to arsine, separation and removal of H₂O and evolved CO₂ from the gas stream, and preconcentration of arsine in the cold trap. Evolved H₂ is separated from AsH₃ as H₂ passes through the cold trap bypassing the ICP. When the temperature of the cold trap is later raised, arsine enters the plasma (free from H₂O, H₂, and CO₂), dissociates, and the resultant atomic arsenic undergoes excitation.

II. RESULTS AND DISCUSSION

A. Direct Product Introduction. Running the reaction without cold trapping or drying agent resulted in immediate extinguishing of the plasma due to the excessive quantities of H₂ evolved using 5% BH₄⁻ reagent. Procedures frequently used involving hydride generation and direct introduction of this product into burners for atomic absorption spectrometry (15, 26, 30, 34, 36, 40, 43, 50, 54, 55), appear, therefore, not to be directly appropriate for the 1.2 kW ICP. Kirkbright, et. al. have employed higher r.f. power (≥ 2.7 kW), more dilute reagent (1%), and smaller total instantaneously mixed volumes of sample and reagent to circumvent this difficulty (60,61). Their detection limit was unfortunately only slightly improved over the nebulizer based value of Olson, Haas, and Fassel (1).

B. Cold Trapping and CO₂ Hindrance. Liquid argon was used as coolant in place of liquid nitrogen in the present work to avoid condensing the "sample gas" argon in the cold trap. The plasma was, however, again extinguished when drying agent and cold entrapment were used if pelletized NaBH₄ reagent was employed in making the 5% solution. Observation of a pronounced 516.5 nm C₂ emission just prior to extinction confirmed the suspected presence of large quantities of CO₂ evolved as a reaction by-product. This C₂ emission occurs in the vertical region of the plasma \geq 2 cm above the load coil. MgCO₃ is used as a pelletizing agent in the 98% NaBH₄. When acidified and degassed with argon, large amounts of CO₂ evolve and build up as "dry ice" in the cold trap. This CO₂ is not tolerated as well by the ICP as it is by flames. The preconcentrated CO₂ emerges rapidly to extinguish the plasma upon warming of the trap. Subsequent use of 99% nonpelletized reagent in making the 5% solution and a 1.5 L/min "sample gas" flow rate greatly reduced the CO₂ effect. The plasma then remained intact; however, an intense C₂ emission still occurred, the character of the plasma was altered, and a large transient background signal (see Fig. 2A) obscured any response from 4 ng/mL of added arsenic when the trap was warmed.

C. CO₂ Removal. Addition of the tube of dry NaOH pellets shown in Fig. 1 was the final factor in removing remaining CO₂. The result was successful arsenic detection using the 193.696 nm line and a 0.2 nm spectral bandpass. The C₂ emission \geq 2 cm above the load coil was then totally suppressed for the 98% pelletized NaBH₄ as well as for the more expensive analytical grade at a "sample gas" flow rate of 0.9 L/min. The transient background signal was greatly reduced and desirably large signals then resulted for standards containing 4 ng/mL arsenic (Fig. 2B). The sample volume was 25 mL.

D. Improvement of Line-to-Background Ratio. Fig. 2 illustrated that the line-to-background ratio was far more important in these studies than any signal/noise considerations. Expanded scale response for 0.4 ng/mL arsenic and blank trials (Fig. 3) manifests the persistence of two remaining smaller background signals. Visual observation of the plasma confirmed that the momentary reduction in size of the traditional ICP "doughnut hole" raises the plasma background and accounts for the initial transient signal upon sudden removal of the cold trap from the coolant dewar. This initial transient is much more pronounced if larger trap volumes than the 26 cm length of 3.17 mm o.d. stainless "U" are cooled. Monitoring of the 193.091 nm atomic carbon line during trap warming confirmed that the second background transient is most likely due to organic species that condensed in the cold trap during collection. These species are apparently not removed by the NaOH trap. The stray light increase accompanying the intense atomic carbon emission undoubtedly accounts for the second background transient. Although background correction schemes and/or larger spectrometers could be employed to correct the remaining background, Table II demonstrates that simple exploitation of the spectral bandpass can solve the problem. The second background transient is barely detectable (4X less than in Fig. 3) when a 25 μ m slit is employed, and Table II indicates that it may be neglected since it is less than 1% of the line at the level (4 ng/mL) normally encountered in a 25 mL natural water sample (baseline level). For lower levels than 4 ng/mL, the background appears small and constant enough to measure separately in time (non-automatically) and subtract from all subsequent sample signals. Continued use of the small inexpensive monochromator in non-background corrected mode is thereby permitted. The 228.812 nm line may also be used where no close-lying carbon emissions occur. The initial spike due

to changes in the ICP "doughnut hole" is also reduced at smaller spectral bandpass values even when the gain is increased to maintain constant arsenic response. These effects are the result of the well-recognized nonlinear (2nd power) dependence of continuous-like spectra on the bandpass versus linear dependence of line spectra (65).

For the levels of arsenic encountered in many natural water samples, the carbon background transient is rendered virtually insignificant (< 1% of line) at small bandpass values. Fig. 4 demonstrates that complete time resolution (from the arsenic signal) of the remaining initial background spike (due to changes in the ICP "doughnut hole") is readily accomplished if a short delay is introduced between removal of the liquid argon dewar and immersion of the trap in lukewarm water. Delay periods up to 10 sec have been tried without any emergence of arsine prior to immersing the trap in the water bath and without subsequent loss in precision or sensitivity. When the liquid argon trap is removed, a thin sheet of ice (condensate from atmospheric humidity) appears to form immediately on the exterior of the trap, thereby helping to insulate it from excessive rapid warming. Arsine then remains trapped until the "U" tube is immersed in lukewarm water which rapidly melts the ice film and volatilizes the analyte.

E. Detection Limits and Natural Water Sample Assay. The detection limit was measured according to the analog criteria of Ramirez-Munoz (66) and Dean et. al. (67) to be 0.5 ng arsenic. This represents 0.02 ng/mL in a 25 mL sample and would be as low as 0.005 ng/mL on a 100 mL sample basis (if a larger vessel were used). It should be noted that the present report of 40-160X improvement over the earlier report of 0.8 ng/mL by Kirkbright, et. al. (60), and of the present 100-400X improvement over the report of 2 ng/mL by Olson, Haas, and Fassel (1) is conservative in that it was

achieved with very little optimization. For example, no optimization of gas flow or vertical position was made for arsenic. A very poor responding (RCA 1P28) photomultiplier tube for this wavelength region (193.696 nm) was operated at moderate voltage (700 v). The spectrometer was directly illuminated (no external optics) at an unfavorably large distance of 13 cm. A vertical quartz extension of the outer coolant tube served to attenuate the 193.696 nm As line. This accounts for the unusually low intensity of this line in our system as compared to the 228.812 nm line. Narrow slit values (25-50 μm) were employed in a non-background corrected, inexpensive, small monochromator. A "home-made" low power ICP was used and simple, non-integrated analog readout was employed on a transient peak height basis. The detection limit criterion used herein (66, 67) is conservative. It is approximately a 4σ signal basis (66). The analog time constant employed for these detection limit measurements was such that the overall instrumental full scale readout response time was ~ 0.5 sec. The measured analog signal to noise ratio used to evaluate the limits of detection given herein was taken as the average of five values. However, the values were not found to vary significantly if a greater or fewer number of trials were averaged. The resultant superior arsenic concentration detection limits were seen to occur in spite of the above "disadvantages" and in spite of the absence of further parameter optimization as soon as the basic difficulties involving H_2 , H_2O , CO_2 , and argon condensate (in the cold trap) were overcome. Figs. 2B and 3 demonstrate that arsenic levels (0.5-10 ng/mL) in natural water samples are easily within the newly expanded concentration range of the ICP. Several ground and well water samples from the Tucson, Arizona area were assayed by this procedure and then by atomic absorption. A more conventional hydride preconcentration procedure was used for the AA comparison

determination. The precision was found to be generally $\leq 5\%$ RSD, and the natural water sample determinations of As at the level of 9 ng/mL by ICP were not found to differ significantly from the conventional atomic absorption result. The ICP response is linear to weight of arsenic added and also to concentration if sample volume is held constant.

Although several authors (25, 35, 38, 52, 54, 61) have alluded to chemical species in solution that may interfere with the conversion of arsenite to arsine, these species were apparently not present in our natural water samples in amounts sufficient to cause any significant interference. The interferences that could have resulted if such species had been present in significant amount would be characteristic of the hydride preconcentration in general. These chemical solution interferences should be independent of whether atomic absorption, stripping voltammetry, etc., or the inductively coupled plasma is used as a detector. Means of masking or removing some of these interferences in solution have been presented by several authors (38, 61) and should apply to the present ICP method as well. We did not find such masking to be necessary for our natural water samples, since no significant interferences were encountered in the determination of arsenic in these samples.

The detection limit on an analog signal/2 σ noise basis (66, 67) was not found to be strongly dependent (see Table II) on spectral bandpass or on whether the 193.696 nm or 228.812 nm line was employed. Choice of 0.2 nm bandpass (100 μ m slit) and/or λ 228.812 nm produced signal enhancements of four- and ten-fold (due to the short wavelength cutoff of the vertical quartz coolant tube extension), respectively, when compared with 0.05 nm bandpass (25 μ m slit) and/or λ 193.696 nm. The limiting noise contribution was due to variation of the plasma emission background. It also increased accordingly

by ~ four and ~ ten-fold at 100 μm and 228.812 nm, respectively, producing little or no net improvement in the signal-to-noise ratio or limit of detection. Since the line-to-background ratio was improved at the lesser spectra bandpass, 25-50 μm was maintained as the chosen slit range. Either 193.696 nm or 228.812 nm may be employed as the analytical wavelength.

Samples much smaller than 25 mL may be analyzed by pipetting the sample (or micro-sample) into a 25 mL volume of 1 N HCl. The resultant concentration detection limit will change accordingly, but a 0.5 ng absolute weight detection limit will remain easily achievable making the procedure applicable to a wide variety of clinical and environmental samples of very low arsenic content. Larger samples up to 100 mL may provide concentration detection limits as low as 0.005 ng/mL.

III CONCLUSIONS

Hydride preconcentration has proved to be a relatively inexpensive, viable approach to improving the concentration detection limit of arsenic determinations with the ICP when the effects of H_2 , H_2O , CO_2 , and argon condensate are controlled by separation and removal. The method of CO_2 elimination employed in these studies would preclude exploitation of H_2Se and H_2Te (owing to their small pKa values relative to AsH_3) in a preconcentration approach.

The authors feel that earlier attempts at arsine preconcentration for the ICP have either failed or have been undesirably high in concentration detection limit due to the deleterious effects of evolved H_2 , CO_2 and H_2O vapor. A viable approach to elimination of these problems has been presented for the ICP, and a much improved concentration detection limit for the ICP determination of arsenic has been reported in this work.

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Table I. Experimental Apparatus and Conditions

Plasma Torch	quartz with vertically extended coolant tube - described elsewhere (63)
RF Generator	27 MHz, 1.2 kW input power
Matching Network	Capacitive - described elsewhere (63)
External Optics	none; direct illumination at a distance of 13 cm from monochromator entrance slit
Monochromator	Heath EU-700, 0.35 meter focal length, $f/6.8$, grating: 1180 grooves/mm, 250 nm blaze.
Spectral Bandpass	0.05 - 0.1 nm
Detector	RCA IP28A photomultiplier operated at 700 V ; Heath EU-701-30 power module
Readout	Linear model 355 strip chart recorder
Wavelengths Used	As 193.696 nm As 228.812 nm C 247.856 nm C 193.091 nm C 516.5 nm

Table II. Spectral Bandpass Effects at 193.696 nm

Slit (μm)	Line-to-Background Ratio at 4 ng/mL As Level	Weight (ng)	Detection Limits (Δs)	
			Concentration (ng/mL)	
			25 mL Sample ^a	100 mL Sample ^b
100	28.	0.5	0.021	0.005
50	56.	0.6	0.023	0.006
25	112.	0.7	0.029	0.007

^aValues realized in existing reaction vessel.

^bProjected values for a larger reaction vessel.

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Figure 1. Hydride Preconcentration Apparatus.

Figure 2. A. CO₂ Hindrance.

a,b. = 4 ng/mL As (III) added in duplicate; c. = "blank";
slit is 100 μm; sample volume is 25 mL.

B. CO₂ Removed.

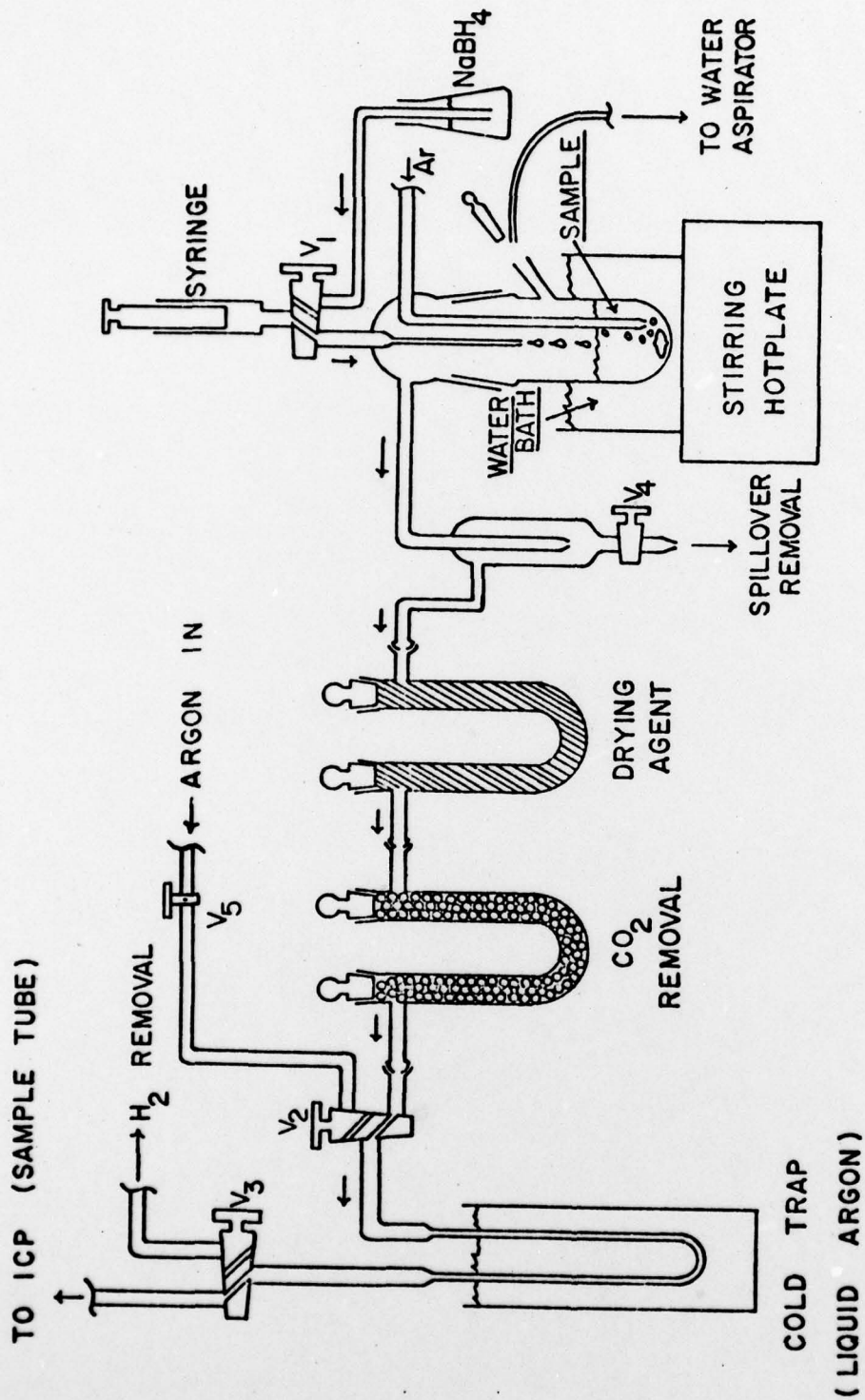
a,b. = 4 ng/mL As (III) added in duplicate; c. = "blank";
slit is 100 μm; sample volume is 25 mL.

Figure 3. Expanded Scale Detection.

a. = 0.4 ng/mL As (III) added in duplicate; b. = duplicate "blanks";
slit is 50 μm; sample volume is 25 mL.

Figure 4. Time Resolution of Remaining Initial Background Transient.

a. = removal of dewar; b. = rapid immersion in lukewarm water;
c. = 2nd removal of dewar; d. = immersion in lukewarm water
following a 3 sec delay; slit is 100 μm; 4 ng/mL As (III) added
to both trials.



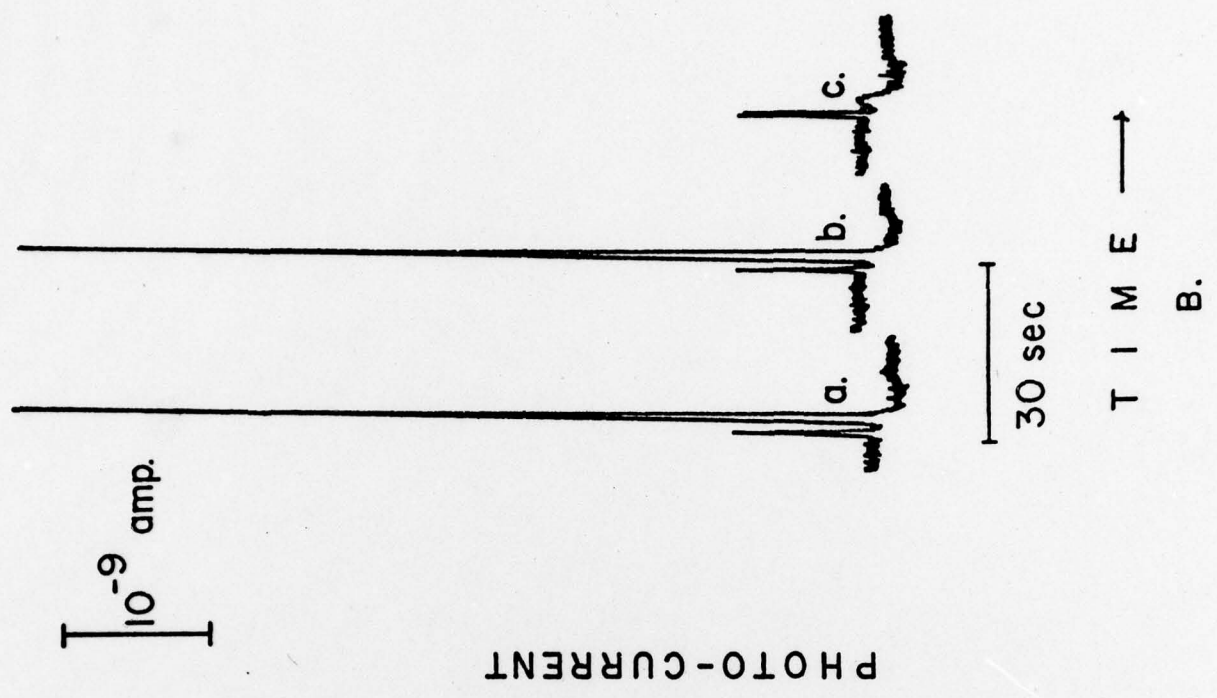
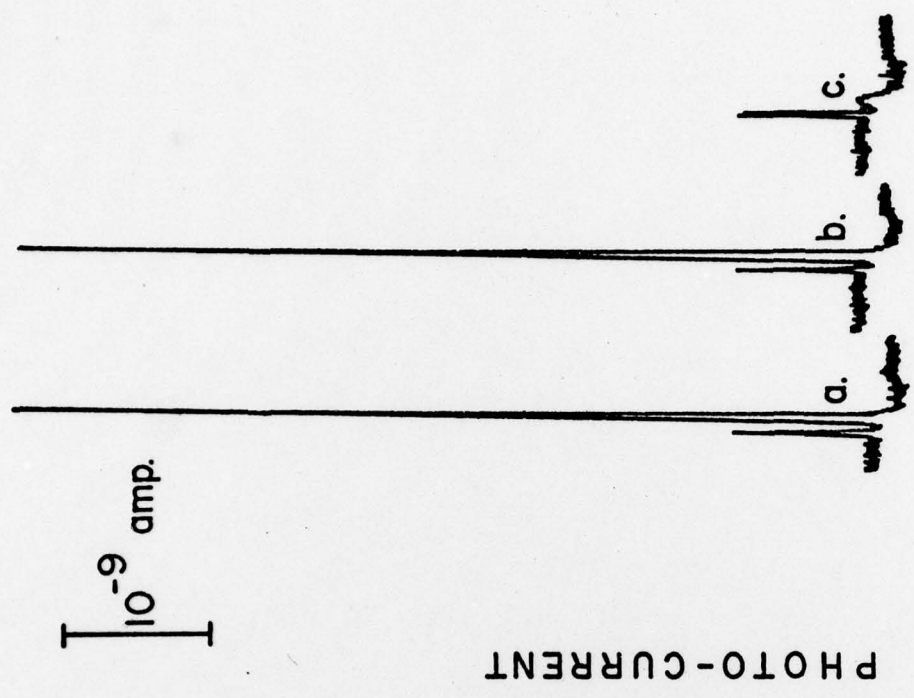
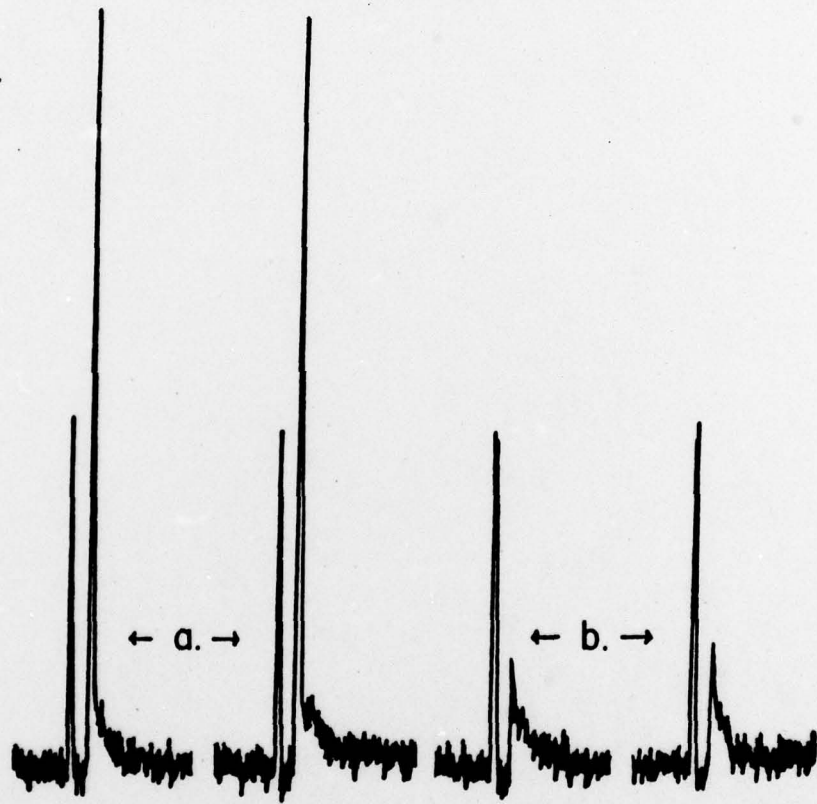


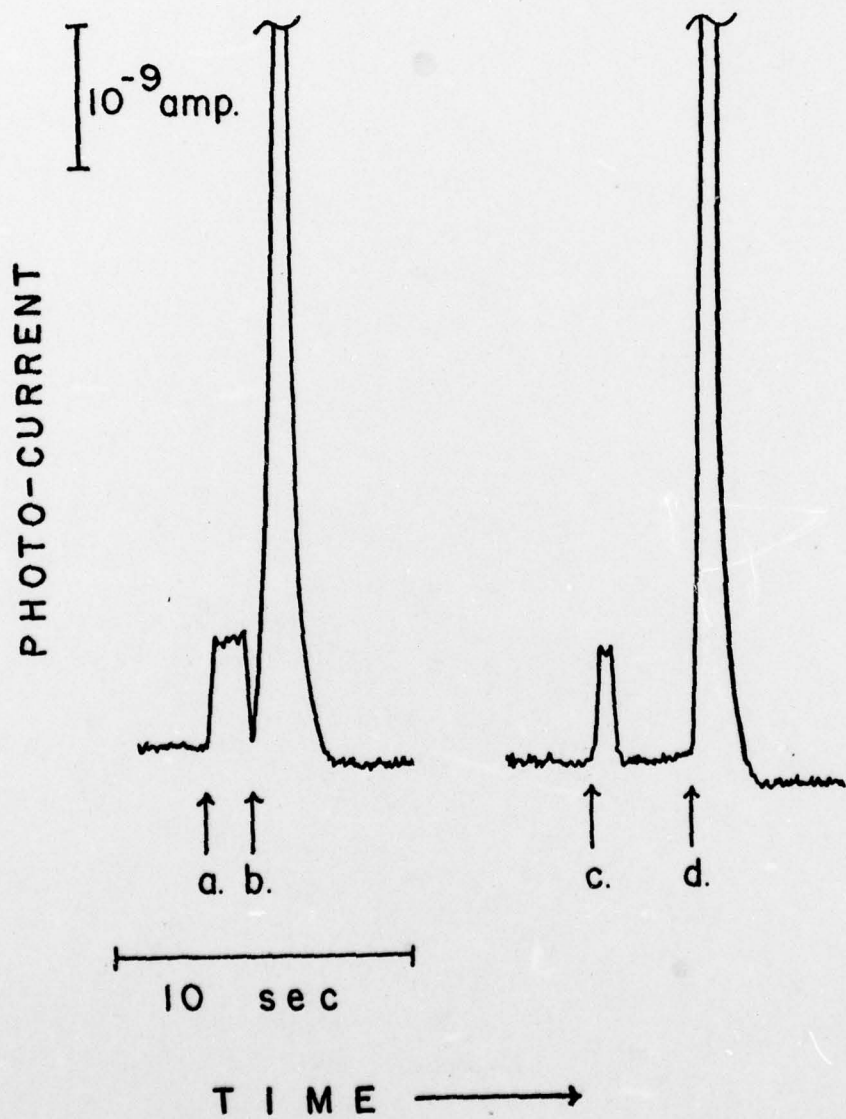
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10^{-10} amp.



30 sec

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