

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231172835>

Interference reduction by L-cystine in the determination of arsenic by hydride generation

ARTICLE *in* ANALYTICAL CHEMISTRY · JUNE 1988

Impact Factor: 5.64 · DOI: 10.1021/ac00162a018

CITATIONS

22

READS

14

5 AUTHORS, INCLUDING:



Ian D Brindle

Brock University

106 PUBLICATIONS 1,874 CITATIONS

SEE PROFILE



X. Chris Le

University of Alberta

248 PUBLICATIONS 7,753 CITATIONS

SEE PROFILE

the development of a specific titration, and (2) the second wave in a strictly anhydrous medium can be considered as characteristic of BV (as in such conditions, the second wave produced by the oxidation of the BR is negligible). However, before this electrochemical method can be used to define a criterion of purity, the electrochemical behavior of the different isomers will have to be specified. We must remember that different isomers appear following the opening point of the heme ring (IX α , IX β , IX γ , IX δ) while the others appear under the effect of light and are amplified during phototherapy (IX α ZZ, IX α ZE, IX α EE); in addition some of these can be esterified (1).

Registry No. BR, 635-65-4; BV, 114-25-0; DMSO, 67-68-5; Pt, 7440-06-4; NaOH, 1310-73-2.

LITERATURE CITED

- (1) Brodersen, R. *Acta Paediatr. Scand.* **1977**, *66*, 625.
- (2) Tvaroha, B. *Cas. Lek. Cesk.* **1961**, *100*, 27.
- (3) Tvaroha, B. *Collect. Czech. Chem. Commun.* **1961**, *26*, 2271.
- (4) Tvaroha, B. *Naturwissenschaften* **1961**, *4*, 99.
- (5) Van Norman, J. D. *Anal. Chem.* **1973**, *45*, 1.

- (6) Van Norman, J. D.; Szentirmay, R. *Anal. Chem.* **1974**, *46*, 11.
- (7) Van Norman, J. D.; Humans, M. M. *Anal. Chem.* **1974**, *46*, 7.
- (8) Siffstein, Ch.; Ariel, M. *Electroanal. Chem.* **1973**, *48*, 447-463.
- (9) Siffstein, Ch.; Ariel, M. *J. Electroanal. Chem.* **1977**, *75*, 551-564.
- (10) Thoma, R. K.; Akingbe, O. *Clin. Chem. (Winston-Salem, N.C.)* **1981**, *27*, 1295-1299.
- (11) Moussa, F.; Kanoute, G.; Levillain, P.; Trivin, F. Communication to 3rd Afr. Med. Meet Cong. Chem., Seville, Sept 1986.
- (12) Winsten, S.; Cehelyk, B. *Clin. Chim. Acta* **1969**, *25*, 441.
- (13) Fitch, P.; Gargus, A. G. *Int. Lab.* **1986**, (Sept), 100.
- (14) With, T. K. *Bile Pigments*; Academic: New York, 1968.
- (15) McDonagh, F.; Lightner, D. A.; Wooldridge, T. A. *J. Chem. Soc., Chem. Commun.* **1979**, 110.
- (16) Braslavsky, S. E.; Holzwarth, A. R.; Schaffner, K. *Angew Chem., Int. Ed. Engl.* **1983**, *22*, 656-674.
- (17) Murao, S.; Tanaka, N. *Agric. Biol. Chem.* **1981**, *45*, 2383-2384.
- (18) Dumas, B. T.; Perry, B.; Jendrejczak, B.; Davis, L. *Clin. Chem. (Winston-Salem N.C.)* **1987**, *33*, 1349-1353.
- (19) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980; Chapter 11, p 466.
- (20) Gros, M. *Réactions électrochimiques. Applications*; Les Houches: 1978; Vol. 2, Chapitre 5.

RECEIVED for review October 14, 1987. Accepted February 1, 1988.

Interference Reduction by L-Cystine in the Determination of Arsenic by Hydride Generation

Charles Boampong, Ian D. Brindle,* Xiao-chun Le, Lev Pidwerbesky, and Claudio M. Ceccarelli Ponzoni

Chemistry Department, Brock University, St. Catharines, Ontario L2S 3A1, Canada

Interference in the production of arsine from As(III) and As(V) by a number of transition elements has been eliminated by the use of a 3% solution of L-cystine in 5 M hydrochloric acid. With this modification, arsenic can readily be determined at low levels in the presence of up to 10 000 $\mu\text{g mL}^{-1}$ of cobalt(II), copper(II), iron(II) and -(III), and nickel(II). At this level, the signal was reduced by less than 10%. Interference from silver(I), mercury(II), and platinum(IV) is eliminated at levels up to 1000 $\mu\text{g mL}^{-1}$. Severe interferences from gold(III) and palladium(II) could not be eliminated above 10 $\mu\text{g mL}^{-1}$ for gold(III) and 1 $\mu\text{g mL}^{-1}$ for palladium(II). In the case of mercury(II), a strong memory effect, in addition to the interference effect, was eliminated by the use of L-cystine. Determinations of low levels of arsenic in standard reference iron and steel by the standard addition method gave excellent results. The results also showed that standard addition need only be used for the most precise work.

The formation of arsine as a way to isolate and concentrate arsenic from an aqueous medium has been described for atomic absorption spectrometry (AAS) (1-3), inductively coupled plasma atomic emission spectrometry (ICP-AES) (3, 4), and direct current plasma atomic emission spectrometry (DCP-AES) (5, 6). Authors have usually stressed the advantages of this method because of its high sensitivity and relative simplicity. However, hydride generation techniques are prone to interferences that can stem from the hydride production and transport processes (7).

Since Smith carried out a general survey of interference by 48 elements on the determination of antimony, arsenic, bismuth, germanium, selenium, and tin (8), a number of papers have been published on interference effects. Quantitative data were determined by Pierce and Brown (9) for various concentrations of interferants and, in a later paper, these authors discussed the radical differences in the interfering effects which derived from the method of generation of the hydride and the mode of production of the atomized arsenic in the beam of the atomic absorption spectrometer (10). Kirkbright and Taddia (11) observed that, without prior separation from interfering elements, the determination of arsenic may be impossible. Thus nickel(II), platinum(IV), and palladium(II) reduced the signal from arsenic completely. In a study of interference, Hershey and Keliher (12) observed that 19 from a total of 50 elements produced an interference effect greater than 10%. Cobalt(II), nickel(II), palladium(II), and platinum(IV) reduced the signal severely. It appears that transition-metal ions are the strongest interferants in the determination of arsenic by this method.

The mechanism of interference has been the subject of considerable discussion. It has been proposed by Welz and Melcher (13-15) that the interference is related to the precipitation of the interfering element. Thus the precipitation of a transition element prior to complete reduction of As(V) is described as producing a gas-solid reaction in which the arsine is decomposed following adsorption onto the finely divided metal. On the other hand, a recent paper by Aggett and Hayashi (16) suggests that interference occurs in solution via the formation of a soluble species formed between the interferant in a low oxidation state, stabilized by the tetrahydroborate(III), and the arsine. In the paper, the authors

support this conclusion with the evidence that arsine can be readily regenerated from the same solution by the sequential addition of an interference reducing reagent and additional sodium tetrahydroborate(III) solution.

Various reagents have been used to reduce or eliminate interferences in the determination of arsenic. Most of the compounds are Lewis bases and could behave as ligands; some are also reducing agents. Belcher et al. (17) reported that ethylenediaminetetraacetic acid (EDTA) reduced the interference from cobalt, iron, nickel, zinc, etc. Aggett and Aspell (18) reported that acetate and citrate ions behave in a similar fashion to EDTA. Guimont et al. (19) observed that thiocyanate ion was better able to reduce interference than either cyanide ion or EDTA. However, with sediment nickel concentrations over 500 ppm, signal reduction was observed that required a mathematical correction based on a linear relationship between nickel concentration and arsenic recovery. Dornemann and Kleist (20) investigated a number of chelating agents with a view to eliminating the interfering effects of cobalt, copper, and nickel. They reported that pyridine-2-aldoxime was more efficient than EDTA or 2,2'-dipyridyl. Peacock and Singh (21) reported that thiourea is extremely effective in reducing interferences from a wide range of elements. Unfortunately, high blank readings make the method unreliable for the determination of trace concentrations of arsenic.

Iron(III) has been used as a releasing agent for the determination of arsenic (13) and selenium (22). In both cases, the authors suggest that the iron behaves as an oxidizing agent and the reduction of iron(III) to iron(II) is kinetically favored over the reduction of, say, nickel(II) to nickel (0). Thus the formation of the hydride is essentially complete before the strongly interfering, low oxidation state nickel has had an opportunity to form and interact with the arsine. Similar logic has been used in rationalizing the partial reduction of interferences by the use of mercury(II) in the generation of germane from a solution containing 1000 $\mu\text{g mL}^{-1}$ of cadmium(II) (23). It is clear that these experimental results would support both the interelement compound formation mechanism and the finely divided metal adsorption mechanism.

L-Cystine was chosen as a reagent that might have an effect on the interference from transition metals. The presence of the disulfide group, which is easily reduced, was thought to be a candidate for the type of competition for the reducing agent mentioned above. L-Cystine is cheap and readily available, gives a low blank for arsenic, and has much lower toxicity than, for example, thiourea.

EXPERIMENTAL SECTION

Instrumentation. Data were acquired with a Spectraspan V dc plasma atomic emission spectrometer equipped with a Beckman hydride generator modified as described elsewhere (6). Signals were recorded on a Fisher Recordall Series 5000 chart recorder. A Brinkmann variable volume Macro-Transferpette was used for all analyte injections with the volume fixed at 5.0 mL.

The arsenic emission line at 193.7 nm was used with an entrance slit of 50 μm (horizontal) and 300 μm (vertical) and exit slit of 100 μm (horizontal) and 300 μm (vertical). Photomultiplier voltage and gain settings were used to provide convenient signals and to minimize noise.

Reagents. Argon of welding grade (Union Carbide, Canada) proved to be sufficiently pure for use without further treatment. All inorganic chemicals were analytical reagent grade or better. L-Cystine was obtained from Sigma (Sigma grade) and BDH. Sodium tetrahydroborate(III) (4% solution) was prepared in 0.1 M sodium hydroxide and was filtered before use. Arsenic(V) solutions (1000 $\mu\text{g mL}^{-1}$) and arsenic(III) (1000 $\mu\text{g mL}^{-1}$) solutions were prepared from $\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$ and As_2O_3 , respectively. Since the As(V) solution was prepared from a nonstandard reagent, the concentration was verified by comparison with the

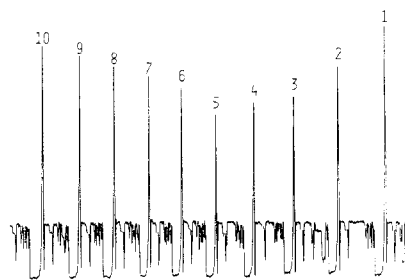


Figure 1. Interfering effect of mercury(II) ($10 \mu\text{g mL}^{-1}$) on the signal from 50 ng mL^{-1} arsenic(V). Peak 1 is the standard 50 ng mL^{-1} As(V). Peaks 2–5 show the signals from 50 ng mL^{-1} As(V) in the presence of $10 \mu\text{g mL}^{-1}$ Hg(II). Peaks 6–10 illustrate the memory effect as the original peak height of the standard 50 ng mL^{-1} As(V) is recovered after several samples are separately reduced and stripped from solution.

As(III) solution, prepared from standard arsenic(III) oxide, in the dc plasma spectrometer. Solutions for the determinations were subsequently prepared by dilution with 5 M hydrochloric acid solution with or without 3% L-cystine.

Procedure. The arsenic solution (5.0 mL, 50 ng mL^{-1}) was added to the reaction vessel. Interferant solution (1.0 mL) was added. Sodium tetrahydroborate(III) solution (1.0 mL) was added and the reaction was allowed to proceed for 30 s before argon was passed through the solution to strip the arsine from the vessel and pass it to the plasma. After the determination was complete, the reduced solution was drained from the reaction vessel. The signals were measured as peak heights.

Sample Dissolution for Iron and Steel. Approximately 0.2–1 g of sample was weighed accurately. The sample was dissolved in 20 mL of 1/1 nitric acid–water solution and then transferred to a 500-mL volumetric flask. The solution was diluted to the mark with deionized water. A 10-mL aliquot of the sample solution was transferred to a 100-mL volumetric flask and diluted to the mark with a solution of 3% L-cystine in 5 M hydrochloric acid.

RESULTS AND DISCUSSION

Acid Concentration. Hydrochloric acid at high concentration reduces interference for some elements. Thus, 5 M hydrochloric acid has a negligible effect on the arsenic signal but improves the recovery of arsenic in the presence of iron and copper compared with similar determinations in 1.4 M HCl. These results are in good agreement with the results of Aggett and Aspell (18) and Hershey and Keliher (12). Further, hydrochloric acid at high concentration effectively eliminates interference from cadmium at the 1000 $\mu\text{g mL}^{-1}$ level (Table I). In the cases of copper and cadmium, formation of the tetrachloro complexes may have an influence on the ability of these species to be reduced. Although high levels of hydrochloric acid in the solution may produce instability in ICP systems, no such problems were encountered in this work.

Effect of L-Cystine. The effectiveness of a solution of 3% L-cystine in 5 M HCl on the reduction of interferences is clearly demonstrated in Table I. Thus interferences from cobalt(II), copper(II), iron(II) and -(III), nickel(II), and zinc(II) at concentrations of up to 10000 $\mu\text{g mL}^{-1}$ are effectively eliminated. Particularly noteworthy is the almost complete elimination of interference from nickel(II).

Mercury(II) interference is problematical in the absence of L-cystine. After an initial determination of a solution containing 50 ng mL^{-1} As(V), as well as $10 \mu\text{g mL}^{-1}$ Hg(II), which gave a relatively good response, repetitive determinations of arsenic in the presence of $10 \mu\text{g mL}^{-1}$ Hg(II) resulted in a steadily diminishing arsenic signal. A memory effect was observed as the arsenic signal slowly recovered over a series of reduction/stripping cycles in the absence of mercury(II) (see Figure 1). A similar effect was observed with iron(III) but only at the 10000 $\mu\text{g mL}^{-1}$ level. In the case of mercury(II),

Table I. Recovery of 50 ng mL⁻¹ of As(V) from Solutions of Transition Metals

element	concn, $\mu\text{g mL}^{-1}$	without L-cystine 1.4 M HCl, % recovery (24)	without L-cystine 5 M HCl, % recovery \pm SD (n)	with L-cystine 5 M HCl, % recovery \pm SD (n)
Fe(II)	1000	n.d. ^a	108 \pm 4 (3)	97 \pm 4 (4)
	10000	— ^b	106 \pm 4 (3)	96 \pm 6 (3)
Fe(III)	1000	n.d.	108 \pm 1 (3)	103 \pm 2 (5)
	10000	—	61 \pm 8 (8) ^c	105 \pm 6 (5)
Co(II)	1000	n.d.	81 \pm 1 (3)	100 \pm 1 (3)
	10000	—	n.d.	91 \pm 1 (3)
Ni(II)	1000	n.d.	2.8 \pm 0.8 (3)	99 \pm 2 (3)
	10000	—	n.d.	95 \pm 1 (3)
Cu(II)	10000	15	100 \pm 6 (3)	102 \pm 3 (3)
	10000	—	82 \pm 5 (3)	91 \pm 3 (3)
Zn(II)	1000	—	107 \pm 4 (3)	101 \pm 3 (3)
	10000	—	108 \pm 1 (3)	93 \pm 2 (3)
Pd(II)	1	—	13 \pm 1 (3)	82 \pm 4 (3)
	10	—	n.d.	20 \pm 1 (3)
	100	—	n.d.	n.d.
Ag(I)	10	—	98 \pm 5 (3)	103 \pm 6 (3)
	100	—	91 \pm 1 (3)	101 \pm 7 (3)
	1000	—	92 \pm 1 (3)	95 \pm 1 (3)
Cd(II)	1000	18	92 \pm 8 (3)	99 \pm 6 (3)
	10000	—	80 \pm 3 (3)	68 \pm 3 (3)
Pt(IV)	10	—	87 \pm 2 (3)	101 \pm 5 (3)
	100	—	6 \pm 1 (3)	89 \pm 1 (3)
	1000	—	n.d.	92 \pm 2 (3)
Au(III)	10	—	74 \pm 1 (3)	69 \pm 2 (3)
	100	—	n.d.	5.9 \pm 0.8 (3)
	1000	—	n.d.	n.d.
Hg(II)	10	—	80 ^c	92 \pm 2 (3)
	100	—	76 ^c	89 \pm 5 (3)
	1000	—	88 ^c	100 \pm 2 (3)
	10000	—	62 ^c	64 \pm 3 (3)

^a n.d., not detected. ^b —, not determined. ^c See note in text and figure.**Table II. Calibration and Standard Addition for Arsenic Determination**

NBS Low Alloy Steel 363 (duplicate)
 correlation coefficient: 0.996 (calibration (4 points))
 correlation coefficient: 0.999 (standard addition (6 points))
 calculated concentration (see ref 25): 101 \pm 7 $\mu\text{g g}^{-1}$
 NBS certified concentration: 100 $\mu\text{g g}^{-1}$

NBS Open Hearth Iron 55E (2 replicates)
 correlation coefficient: 0.999 (calibration (4 points))
 correlation coefficient (1): 0.999 (standard addition (6 points))
 correlation coefficient (2): 0.998 (standard addition (6 points))
 calculated concentration (see ref 25): 72 \pm 4 $\mu\text{g g}^{-1}$ (1), 70 \pm 6 $\mu\text{g g}^{-1}$ (2)
 group mean 71 \pm 7 $\mu\text{g g}^{-1}$
 NBS certified concentration: 70 $\mu\text{g g}^{-1}$

it may be that mercury(0) is adsorbed on the desiccant or the walls of the tubing where it can interfere with the transport of the arsine.

Very poor recoveries of the arsenic signal were obtained in the cases of gold(III) and palladium(II). Thus, in the absence of L-cystine, a poor (13%) recovery of the arsenic signal was achieved in the presence of only 1 $\mu\text{g mL}^{-1}$ of palladium(II). Although interference was reduced by L-cystine, and a recovery of 82% was achieved at this level, at 10 $\mu\text{g mL}^{-1}$ Pd(II), the recovery was only 20%.

It was felt that, although As(V) is generally the worst case and that As(V) is reduced to arsine via As(III), a few representative transition elements should be investigated to see if there is a material difference between the interferences on As(V) and As(III) reduction. Results for arsenic(III) closely followed those for arsenic(V) for the selected examples (Ag(I), Cd(II), Co(II), Ni(II), and Pt(IV)).

Determination of Arsenic in Iron and Steel. Determination of arsenic in NBS Standard Reference Open Hearth

Iron 55E and Low Alloy Steel 363 gave excellent results. Standard additions technique was used to determine if there were any systematic interferences with the method. Final concentrations and standard deviations were determined from the standard addition line by the method outlined in Miller and Miller (25) and adapted for use in the EXCEL database program. In the case of the Open Hearth Iron 55E, two replicate determinations were carried out to verify the methodology; in the case of the Low Alloy Steel 363, a duplicate standard addition was performed. The data for the determinations are summarized in Table II. The slopes of the calibration lines and standard addition lines gave recoveries between 94% and 107%. This indicates that there are no systematic interferences in these determinations. Under normal circumstances, there would be no need to carry out the standard addition method for this type of analysis.

CONCLUSION

A 3% solution of L-cystine provides an effective means of reducing interferences from a variety of transition metals in the determination of arsenic. The determination can readily be applied to metallic samples and has good sensitivity.

Registry No. As, 7440-38-2; Co, 7440-48-4; Cu, 7440-50-8; Fe, 7439-89-6; Ni, 7440-02-0; Ag, 7440-22-4; Hg, 7439-97-6; Pt, 7440-06-4; Au, 7440-57-5; Pd, 7440-05-3; Cd, 7440-43-9; L-cystine, 56-89-3; steel, 12597-69-2; arsine, 7784-42-1.

LITERATURE CITED

- Holak, W. *Anal. Chem.* **1969**, *41*, 1712-1713.
- Welz, B. *Chem. Br.* **1986**, *22*, 130-133.
- Nakahara, T. *Prog. Anal. At. Spectrosc.* **1983**, *6*, 163-223.
- Thompson, M.; Pahlavanpour, B.; Walton, S. J.; Kirkbright, G. F. *Analyst (London)* **1978**, *103*, 568-579, 705-713.
- Panaro, K. W.; Krull, I. S. *Anal. Lett.* **1984**, *17*, 157-172.
- Boampong, C.; Brindle, I. D.; Ceccarelli Ponzoni, C. M. *J. Anal. At. Spectrom.* **1987**, *2*, 197-200.
- Dedina, J. *Anal. Chem.* **1982**, *54*, 2097-2102.
- Smith, A. E. *Analyst (London)* **1975**, *100*, 300-306.

- (9) Pierce, F. D.; Brown, H. R. *Anal. Chem.* **1976**, *48*, 693-695.
- (10) Pierce, F. D.; Brown, H. R. *Anal. Chem.* **1977**, *49*, 1417-1422.
- (11) Kirkbright, G. F.; Taddia, M. *Anal. Chim. Acta* **1978**, *100*, 145-150.
- (12) Hershey, J. W.; Kellher, P. N. *Spectrochim. Acta Part B* **1986**, *41B*, 713-723.
- (13) Welz, B.; Melcher, M. *Analyst (London)* **1984**, *109*, 573-575.
- (14) Welz, B.; Melcher, M. *Analyst (London)* **1984**, *109*, 577-579.
- (15) Welz, B.; Schubert-Jacobs, M. *J. Anal. At. Spectrom.* **1986**, *1*, 23-27.
- (16) Aggett, J.; Hayashi, Y. *Analyst (London)* **1987**, *12*, 277-282.
- (17) Belcher, R.; Bogdansk, S. L.; Henden, E.; Townshend, A. *Analyst (London)* **1975**, *100*, 522-523.
- (18) Aggett, J.; Aspell, A. C. *Analyst (London)* **1976**, *101*, 341-347.
- (19) Guilmon, J.; Pichette, M.; Rhéume, N. *At. Absorpt. Newsl.* **1977**, *16*, 53-57.
- (20) Dornemann, A.; Kleist, H. *Fresenius' Z. Anal. Chem.* **1981**, *305*, 379-381.
- (21) Peacock, C. J.; Singh, S. J. *Analyst (London)* **1981**, *106*, 931-938.
- (22) Bye, R. *Analyst (London)* **1986**, *111*, 111-113.
- (23) Brindle, I. D.; Ceccarelli Ponzoni, C. M. *Analyst (London)* **1987**, *112*, 1547-1550.
- (24) Boampong, C., unpublished results.
- (25) Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*; Wiley: New York, 1984; pp 82-107.

RECEIVED for review October 6, 1987. Accepted February 1, 1988. The Fondation Gran Mariscal de Ayacucho of Venezuela is thanked for providing a graduate scholarship to C. M.C.P. The Canada Department of Employment and Immigration is thanked for providing a summer studentship (Challenge '87) for L.P. Funds for the purchase of the Spectraspan V were provided by the Government of Ontario BILD program.

Dual-Beam Absorbance Measurements by Position-Sensitive Detection

Curtiss N. Renn and Robert E. Synovec*

Department of Chemistry, BG-10, Center for Process Analytical Chemistry, University of Washington, Seattle, Washington 98195

A simple, reliable, and rugged absorbance detector has been designed and tested that employs a position-sensitive detector with a dual-beam optical arrangement. The mathematical formulation for optical and electronic null conditions is presented and experimentally observed as optimum. The device requires a single detector and no moving parts, ideal for process analysis conditions or general application. An absorbance level of 6×10^{-5} AU ($3 \times$ root mean square) was achieved with the microbore high-performance liquid chromatographic separation of the two isomers of FD & C Blue Dye 2 using a HeNe laser source and the absorbance detector with a capillary flow cell. Possibilities for simultaneous refractive index (RI) monitoring or, conversely, RI effect reduction are discussed.

Molecular absorbance spectroscopy is a popular tool of the analytical chemist. Much has been reported in terms of static solution measurements (1, 2), and flowing solution measurements (3, 4), i.e., with high-performance liquid chromatography (HPLC) and flow injection analysis (FIA). In the context of HPLC, one is generally interested in determining the identity and quantity of certain sample components, in relation to some analytical problem or condition. Molecular absorbance in the ultraviolet to visible portion of the spectrum (UV-vis) is a highly sensitive technique for many chemical species of interest and when coupled with HPLC affords a fair level of selectivity via wavelength selection (5, 6). The common modes of absorbance detection employ fixed-wavelength, variable-wavelength (scanning), or multichannel (photodiode array) detectors (7). If improved solute detectability is a concern, many laser-based approaches to HPLC and FIA absorbance detection have been developed based upon thermal lens spectroscopy (8-18), Fabry-Perot interferometry (19), indirect polarimetry (20), and high-frequency amplitude modulation (21, 22). In each of these laser-based methods, quantitative analysis is ultimately limited by some

form of noise. Often the laser is the culprit, by limiting either detectability or precision in the measurements due to laser "flicker" noise. Signal processing and the translation to solute properties are often highly variable and "system" dependent for many of these laser-based approaches.

Absorbance detection is quite popular for process control applications, where the analytical instrumentation should be not only sensitive and selective but also rugged, reliable, and relatively inexpensive to purchase and maintain (23, 24). Though excellent in terms of absolute solute detectability, many of the laser-based absorbance detectors require more development, in terms of the requirements for process control applications. This paper deals with a novel development, in which a dual-beam arrangement, that is conventionally utilized for optimized absorbance detection to ensure precision and accuracy in quantitation, is employed with a position-sensitive detector (PSD), which is conventionally applied in optical alignment. The development is a dual-beam absorbance detector, with excellent signal and noise characteristics, ideal for process control.

The approach to dual-beam absorbance detection employs a PSD which has two distinct advantages relative to other approaches. First, a single detector is employed which is inherently uniform in performance characteristics, in contrast to dual-photodiode systems which suffer from temperature and electronic fluctuations and light response differences (6). Dual-photodiode systems are more difficult to prepare and maintain as compared to the PSD system described here.

Second, both electronic and optical nulls are employed with the dual-beam PSD absorbance measurement which improves detector reliability and function. It is accomplished without any moving parts, i.e., mechanically, which must be avoided for process instrumentation if at all possible. Light source modulation has conventionally been accomplished mechanically. Recently, optoacoustic modulation was incorporated in a dual-beam absorbance detector, coupled with a single photodiode and signal processing via demodulation (21). This system is presently too costly and cumbersome for minia-