United States
Environmental Protection
Agency

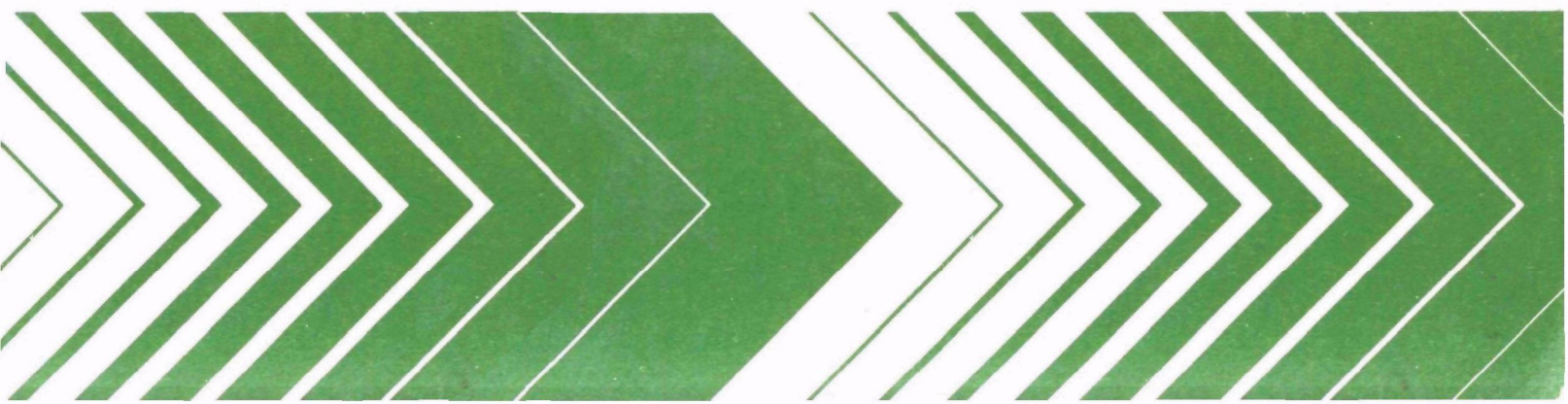
Environmental Research
Laboratory
Athens GA 30605

EPA-600/4-80-020
March 1980

Research and Development

EPA

Ion Chromatography of Anions



RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/4-80-020
March 1980

ION CHROMATOGRAPHY OF ANIONS

by

Thomas B. Hoover
and
George D. Yager
Analytical Chemistry Branch
Environmental Research Laboratory
Athens, Georgia 30605

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30605

DISCLAIMER

This report has been reviewed by the Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure chemical pollutants in the environment. The Analytical Chemistry Branch of the Athens Environmental Research Laboratory develops techniques for identifying and measuring chemical pollutants in water and soil.

This report evaluates a relatively new technique, ion chromatography, for the measurement of anionic species in water, using commercial instrumentation. It will acquaint administrators and researchers with the analytical capabilities of the technique.

David W. Duttweiler
Director
Environmental Research Laboratory
Athens, Georgia

ABSTRACT

A Dionex Model 10 Ion Chromatograph was evaluated for the measurement of anionic species in water. The theoretical effect of hydrogen ion activity (pH) on the elution time of phosphate and arsenate was tested and empirical selectivity coefficients were determined for the major protolytic species of these acids. Calibration curves were obtained for arsenate, bromide, chloride, nitrate, nitrite, phosphate, selenate, selenite, and sulfate by direct injection of 0.1 mL of standards and, in most cases, by preconcentration of 5 to 50 mL of solution on the ion exchange concentrator columns available from the instrument manufacturer. Detection limits for ions other than chloride were approximately 0.2 µg independent of the method of sample introduction. For chloride the detection limit was 2 ng, by direct injection. The concentrator column permitted determination of any of the above ions at concentrations greater than 10 µg/L.

CONTENTS

FIGURES

TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

min.	- minute
mL	- milliliter
mm	- millimeter
mM	- millimolar
ppb	- parts per billion
µg	- microgram
µm	- micrometer
µmho/cm	- micromhos per centimeter

SYMBOLS

A^{-2}, A^{-3}	--	contributions of doubly- and triply-charged species, respectively, to the retention time of a tribasic acid
As	--	arsenic
C_1, C_2, C_3	--	selectivity coefficients of protonated species having 1, 2, or 3 charges, respectively
E	--	molarity of eluent ion
H	--	recorder peak height
H^+	--	hydrogen ion activity
HPO_4^{2-}	--	hydrogen phosphate anion
$H_2PO_4^-$	--	dihydrogen phosphate anion
K_1, K_2, K_3	--	successive protolysis constants of a tribasic acid
pH	--	negative logarithm of hydrogen ion activity
PO_4^{3-}	--	orthophosphate anion
Se	--	selenium
T	--	retention time

SECTION 1

INTRODUCTION

Improved analytical methods for inorganic anionic species in water are needed both because the oxidation state, ionization, and complexation of most of the heavy elements have a critical influence on their distribution, cycling, and transport in the environment and because the human health effects of many elements seem to be most clearly related to specific anionic species (1). Sawicki (2) has indicated that the common atmospheric anions--arsenate, arsenite, chromate, nitrate, nitrite, selenate, selenite, sulfate, and sulfite--have all been implicated as carcinogenic, mutagenic, co- or pre-carcinogenic. These ions may be equally significant as water pollutants.

Ion chromatography is a relatively recent analytical development that appears especially promising for the determination of aqueous anions. It has already become established for the analysis of airborne particulates (3,4). This development depends on the successful application of the conductivity detector to ion exchange chromatography. The principle, described by Small, Stevens, and Bauman (5) utilizes a so-called suppressor column following the ion exchange separator column to convert the eluent ions to a form that makes little contribution to the specific conductance of the final discharge. Although the principle has been applied to a variety of systems, it has been most successful with a carbonate-bicarbonate reagent used to elute selectively a series of anions. In the cationic exchange suppressor column the eluent is converted to carbonic acid, which makes a consistent, small contribution to the background conductance. Analyte anions, as they come through the system individually, are converted to the corresponding acids and are registered as sharp increases in conductance.

Ion chromatography offers several major advantages for water analysis.

- It is especially applicable to the determination of the anions of strong acids, for which there are few alternate, general, sensitive methods.

- The non-specific nature of conductometric detection allows several ions to be determined in the same sample and permits extension of the procedure to many ionic species.

- Conductometric detection is highly sensitive and relatively free of interferences.

- The technique permits the determination of different stable valence states of the same element.

On the other hand, some limitations need to be considered in any application of ion chromatography.

- Because of the non-specific nature of the detector the chromatographic peaks are identified only by their retention times.

- In common with other column chromatographic techniques, the system gives peaks that broaden appreciably with increasing retention time. At present, ion chromatography has no compensatory techniques, such as temperature programming or gradient elution.

- To provide a practicable working life for the suppressor column between regenerations, the separator column has a very small exchange capacity. Sample injections are limited to a few microequivalents of exchangeable ions and a volume usually less than one mL.

This report presents a preliminary evaluation of ion chromatography and gives calibration data for nine anions both by direct injection of aqueous standards and by preconcentration on small ion exchange columns.

SECTION 2

CONCLUSIONS

Ion chromatography is a convenient and dependable instrumental technique for the separation and measurement of several anions in water samples.

The detection limit for the ions studied in this report (arsenate, bromide, nitrate, nitrite, phosphate, selenate, selenite, and sulfate) is about 0.2 µg.

Concentrator columns provide the reproducible collection of trace anions from 50 mL or more of water, permitting the measurement of concentrations greater than 10 ppb.

SECTION 3

RECOMMENDATIONS

Further work needs to be done with environmental samples to assess the extent and impact of interferences in complex samples. Because peak identification in ion chromatography is made by retention time, a reliable means of detecting co-eluting peaks is needed, and rapid, simple methods of confirming peaks are desirable.

For trace analysis and speciation of environmental samples, lower detection limits are needed. This probably entails improved precision through closer temperature control of the separator and detector, reduction of dead volume, and more reproducible loading of concentrator columns.

Improved analytical methods should be developed for the anions of weak acids, which are not sensitively measured by conductance.

SECTION 4

EXPERIMENTAL PROCEDURES

EQUIPMENT

A Dionex Corporation Model 10 Ion Chromatograph was used. This model requires manual sample injection and has a single analytical train of separator and suppressor columns. Ion exchangers used in various combinations were: Anion Precolumn (3 x 150 mm), Anion Separator (3 x 150 and 3 x 500 mm), Suppressor (6 x 250 mm), and several Anion Concentrators (3 x 50 mm).

Flow rate was usually recorded as percentage of full output of the eluent pump (30% in most cases). During the study, the control knob on the eluent pump became loose and had to be reset. The pump was calibrated with eluent flowing through a 500-mm separator and the suppressor columns.

The original 0.1 mL sample injection loop was used as supplied, without calibration. Sample volumes loaded onto the concentrator columns were measured by the markings on 25- and 50-mL disposable syringes driven by a Harvard Apparatus infusion pump (Model 975) at 0.5-1.0 mL/min. In later runs, the effluents from the concentrator columns were collected in volumetric flasks.

The suppressor column was regenerated, usually daily, according to the manufacturer's recommendation. The semi-automatic schedule used a 15-min. regeneration cycle followed by a 30-min. rinse.

MATERIALS

Laboratory reverse-osmosis water was deionized in a three-column Illinois Water Treatment system and used for all solutions. Reagent solutions (eluents, regenerant, and standards) were filtered through 0.45-μm Millipore cellulose acetate-nitrate membranes. Stock solutions of anions (1000 mg/L) were prepared from reagent-grade chemicals and were not purified or independently assayed, except for sodium nitrite. The nitrite stock solution was titrated into standard potassium permanganate-sulfuric acid as recommended by Kolthoff and Belcher (6). The indicated assay of the nitrite (80.5%) was used in subsequent calculations.

The Dionex recommended eluent of 2.4 mM sodium carbonate - 3.0 mM sodium bicarbonate is referred to as the "standard eluent" in this report. Other eluent compositions are defined as they are referred to.

SECTION 5

RESULTS AND DISCUSSION

pH EFFECTS

It is well recognized (5) that polybasic acids elute as a single component in anion exchange chromatography, even though the less protonated and more highly charged species are more strongly held by the exchanger. This is true because the dynamic hydrolysis process maintains the equilibrium distribution of species at the pH of the eluent in opposition to the ion exchange tendency to separate the hydrolytic species. Consequently, the retention time of an acid such as phosphoric can be shifted by changing the pH of the eluent. A higher pH increases the proportion of highly charged (deprotonated) species and increases the retention time. The effect is described quantitatively by the following equation, adapted from Rieman and Walton (7) for a doubly-charged eluting ion (carbonate).

$$T \propto \frac{[C_1K_1(H^+)^2/E^{1/2}] + [C_2K_1K_2(H^+)/E] + [C_3K_1K_2K_3/E^{3/2}]}{(H^+)^3 + K_1(H^+)^2 + K_1K_2(H^+) + K_1K_2K_3} \qquad (1)$$

In equation 1 T is the retention time of a tribasic acid having protolysis constants K_1, K_2, and K_3. E is the molar concentration (strictly, activity) of the doubly charged eluent ion and H^+ is the hydrogen ion activity of the eluent. C_1, C_2, and C_3 are the respective ion exchange selectivity constants for the singly-, doubly-, and triply-charged hydrolytic species.

The relation of equation 1 was tested using a series of carbonate-bicarbonate eluents of varying pH and carbonate concentration. Table 2 summarizes the data for ortho-phosphate. The column headed E (mM) gives the analytical concentration of carbonate ion in the eluent, in millimoles per liter. The effect of the singly charged bicarbonate ion on the elution was neglected. The third and fourth columns give the calculated contributions of the doubly- (HPO_4^{2-}) and triply-charged (PO_4^{3-}) species to the overall retention time of the component. The contribution of the singly-charged $H_2PO_4^-$ ion was too small to estimate from these data. The selectivity

constants, C_2 and C_3, shown at the bottom of Table 2, were calculated by a least-squares multivariate fit to the last two terms of Equation 1. The quantities A^{-2} and A^{-3} in the table were then calculated from these selectivity constants. The third row of the table shows anomalously poor agreement between the calculated and observed retention times. This same eluent, however, gave consistent results with arsenate and the phosphate retention time measured with it was included in the least-squares fitting of the constants. Although at pH 11 the ionization constants indicate that 96% of the phosphate is in the doubly-charged form, HPO_4^{2-}, Table 2 indicates that the triply-charged species, A^{-3}, determines the retention time.

Corresponding results are shown for arsenate in Table 3. The selectivity constants are not directly comparable to those for phosphate because the latter data were obtained with a 500-mm separator column whereas the arsenate results were obtained with the 150-mm column to keep the retention times conveniently short. Although phosphate and arsenate have very similar ionization constants, the pH effect on retention time is appreciably less for arsenate and only the selectivity constant for the triply-charged species could be reliably estimated from these data.

CALIBRATIONS

General Observations

Instrumental response was measured by the peak height on the recorder chart but converted to specific conductance in this report by use of the nominal cell constant of one mho/cm. Some workers (8,9) have measured peak area, which is more directly related to the quantity of analyte passing through the detector. We compared calibration curves for nitrite, nitrate, sulfate, and arsenate using peak heights, on one hand, and peak areas determined by hand planimetry of the charts, on the other. No significant improvement in detection limits could be ascribed to the areal measurements.

Calibrations for several ions were made both on a concentration basis, using the standard 0.1 mL injection loop, and on a weight basis, collecting the analyte on concentrator columns (10) from varying volumes and concentrations of sample. Table 4 compares some results for phosphate, showing that the ultimate sensitivity is essentially the same on either basis.

TABLE 3. ION CHROMATOGRAPHY DETECTION LIMITS FOR PHOSPHATE

Full-Scale µmho/cm	Direct Injection (0.1 mL) (µg)	Accumulator (5-25 mL) (µg)
1	0.067	0.040
2	0.016	0.039
10	-	0.24
30	0.86	0.80

The different full-scale sensitivities of the instrument appeared to be fully consistent and interconvertible in terms of the specific conductance. Nearly all calibration data were pooled over several sensitivity ranges. Detection limits are given as the quantity of analyte distinguishable from the blank with 95% confidence (11).

Arsenate

The arsenic (V) anion is strongly retained on the separator column, having a long retention time. Hansen et al (12) have recommended a strongly alkaline eluent for arsenate (3.5 mM sodium carbonate plus 2.6 mM sodium hydroxide) that provides good resolution of the arsenate peak from other common anions. This eluent, even on a 250-mm separator column gives a retention time of 22 to 27 minutes. When separation from other interferents is not a problem, the sensitivity of detection can be improved and the retention time shortened by working at a lower pH. (See the section on pH effects.) A calibration curve for As (V) by direct injection of 0.1 mL portions is shown in Figure 1. The eluent was 3 mM sodium carbonate and 3 mM sodium bicarbonate and gave a retention time of 8.7 to 9.0 minutes on the 150-mm separator column. The calibration data are summarized in Table 5.

Bromide

Table 6 presents calibration data for bromide by direct injection on the 500-mm separator column, with standard eluent.

Chloride

Calibration data for the direct injection of chloride standards are summarized in Table 7. Data were pooled for the calculation of the least-squares equation although variances at the different full-scale ranges were not strictly homogeneous.

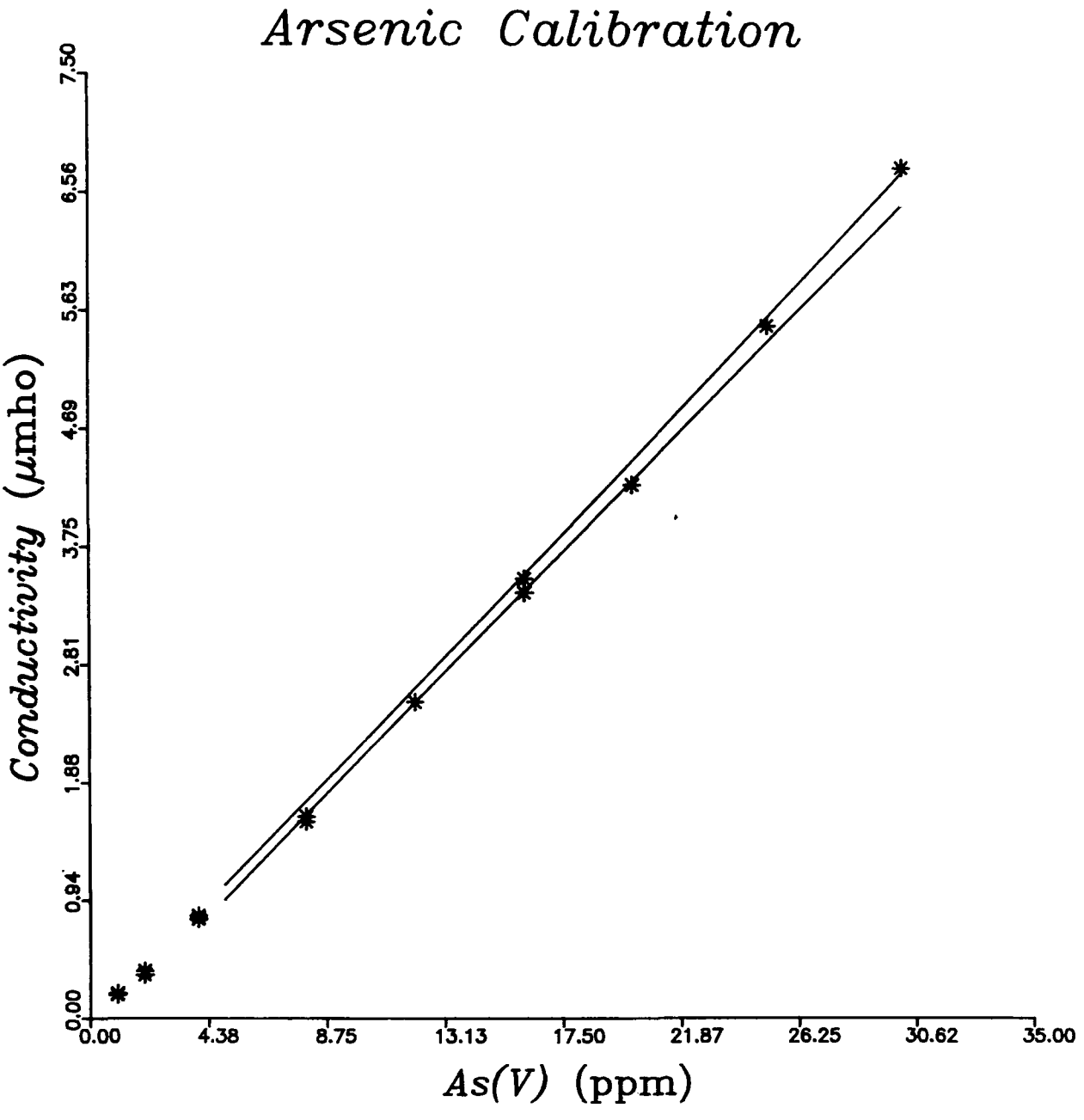


Figure 1. Calibration for arsenic (V).

The negative water peak immediately preceding the elution of the chloride may account for the inhomogeneity, as the standard solutions were not adjusted to the same carbonate strength as the eluent (10).

Nitrate

The nitrate calibration was made by collecting 5 to 40 mL samples of 0.1 to 1000 ppb solutions of nitrate on the concentrator column. A blank correction of 1 µg/L nitrate was estimated from eight runs with 5 to 90 mL of deionized water treated in the same manner as the standards. Even after correction for the blank, the calibration curve had an apparently significant positive intercept. This result may denote a small but consistent source of contamination that was not identified. The results are presented in Table 8 and Figure 2.

Nitrite

The nitrite calibration, summarized in Table 9 and Figure 2, was made with the concentrator column, using 5 to 25-mL volumes of standard solutions containing 6 to 160 µg/L. A peak appearing immediately after the water peak was assumed to be chloride impurity at the time the runs were made. Koch (13) has recently presented evidence that this peak represents oxidation to nitrate in the suppressor column. The data were recalculated in Table 9 using the sums of the two peaks as an approximation to the total response to injected nitrite ion. The correction for the oxidation product varied from 0.2 to 7 µmhos/cm. In Figure 2, the curve for nitrite is much steeper than that for nitrate because the nitrite, eluting sooner, has a much sharper peak and, therefore, provides a higher concentration in the detector cell for the same quantity injected.

Phosphate

The phosphate calibration was made with the concentrator column, collecting 5 to 25 mL of 10 to 100 ppb solutions. The data, presented in Table 10 and Figure 3, reveal a small but significant curvature but negligible intercept.

Selenate

When separated with the standard eluent and a 500-mm separator column the Se (VI) anion has an inconveniently long retention time of 29.2 minutes. A calibration for direct injection *via* the 0.1 mL sample loop and these analytical conditions is presented in Table 11 and the lower curve of Figure 4. A calibration was also made with the 150-mm separator column and an eluent of 1 mM sodium carbonate and 10 mM sodium bicarbonate, providing a retention time of 14.7

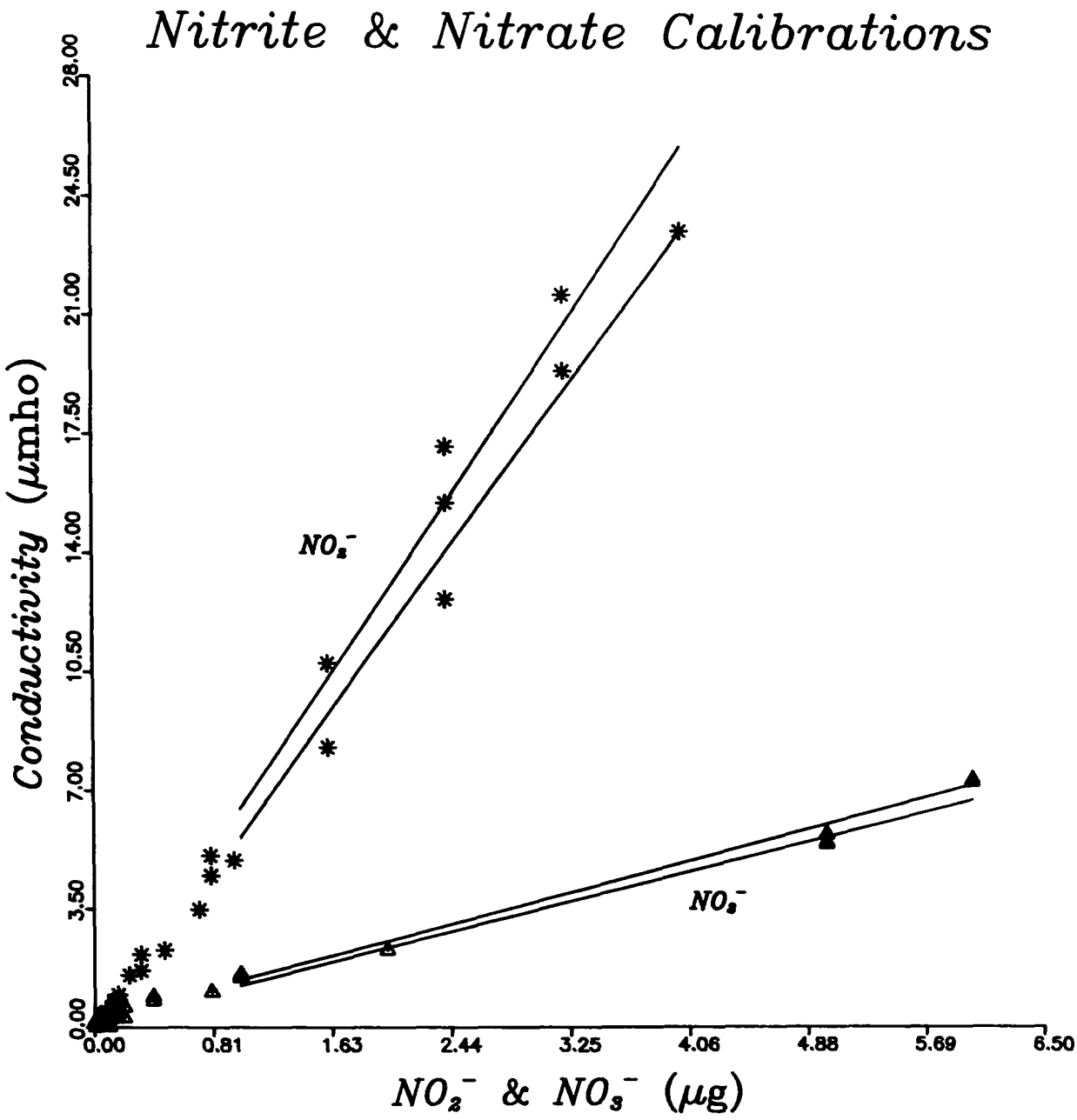


Figure 2. Calibrations for nitrite and nitrate.

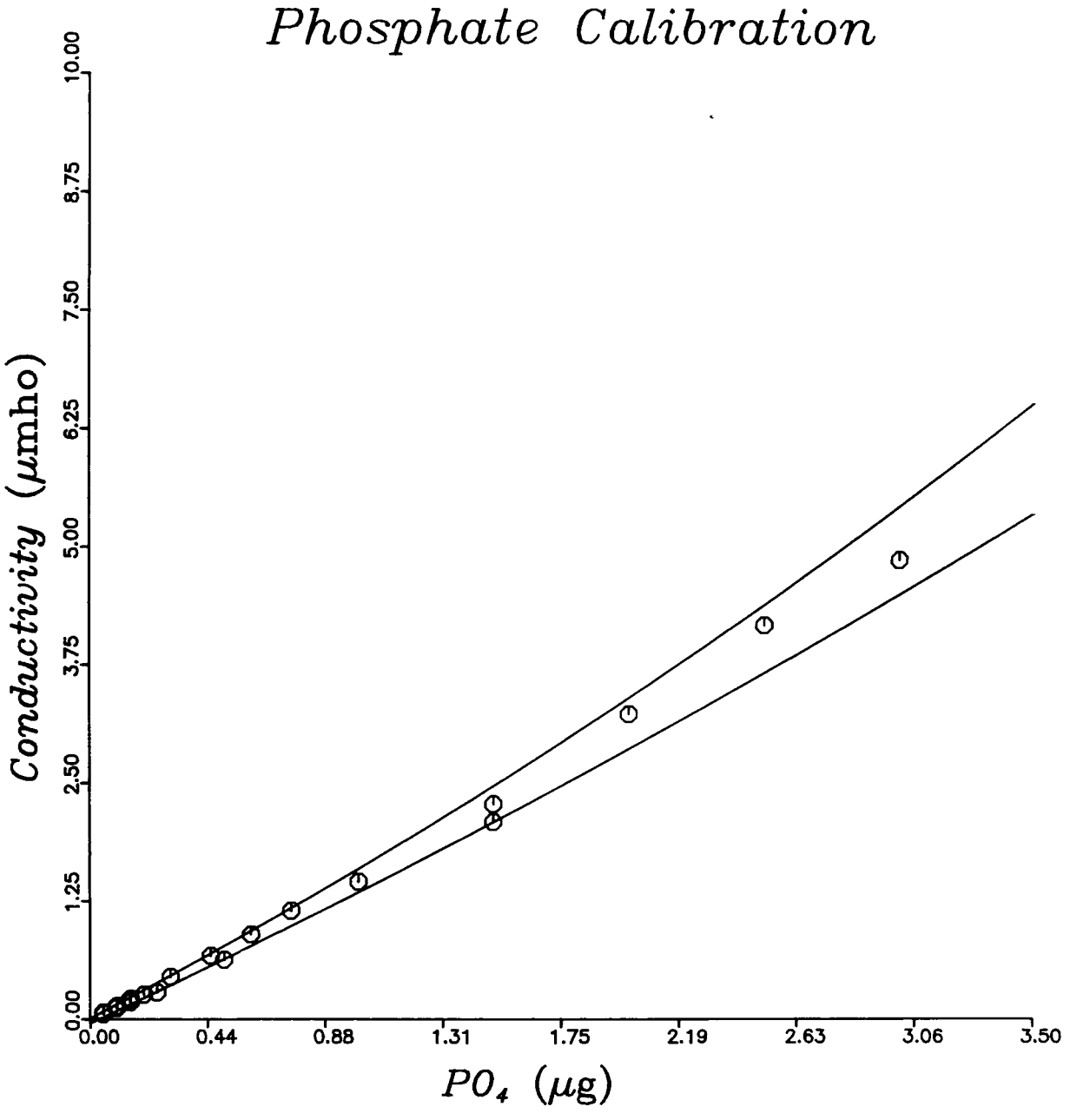


Figure 3. Calibration for phosphate.

minutes. The result, shown as the upper curve of Figure 4, had significant curvature in the range of 0.5 to 25 ppm. The data are summarized in Table 12.

Selenite

A calibration for selenium (IV) anion, made in January 1979, by direct injection of 0.1 mL of standards showed remarkably little scatter and a highly significant curvature over the range 0.1 to 40 ppm. These data are shown as the upper curve of Figure 5 and in Table 13. Five months later, five additional points, presumably run under the same conditions, showed an appreciably longer retention time (7.4 minutes *vs.* 5.9 minutes) and more random error. The latter points were linear over the range of 8 to 27 ppm and extrapolated approximately to the original calibration at lower concentrations. No explanation for the discrepancy has been found.

A calibration using 5 to 50 mL samples collected on the concentrator column and analyzed by the same conditions used previously yielded the same retention time as the first calibration by direct injection and was linear in the range 0 to 2.5 µg. The slope of the latter was slighty less (1.9 µmho/µg *vs.* 2.2 µmho/µg) and the detection limit was higher (0.1 µg *vs.* 0.01 µg). This calibration is presented in Figure 6 and Table 14.

Sulfate

A calibration for sulfate by direct injection is summarized in Table 15. The negative intercept is statistically significant.

Summary

All anions discussed in this report except arsenate were run at the conditions recommended by Dionex: 500-mm separator column, 30% flow (2.56 mL/min.), and "standard" eluent of 2.4 mM sodium carbonate plus 3 mM sodium bicarbonate. The retention times and detection limits observed at these uniform conditions are summarized in Table 16. At retention times greater than 4 minutes, the detection limits were generally in the range 0.1 to 0.2 µg. No distinction in detection limit could be drawn between the direct injection procedure and the use of the concentrator column although the latter permits relatively large samples of much more dilute solutions to be analyzed.

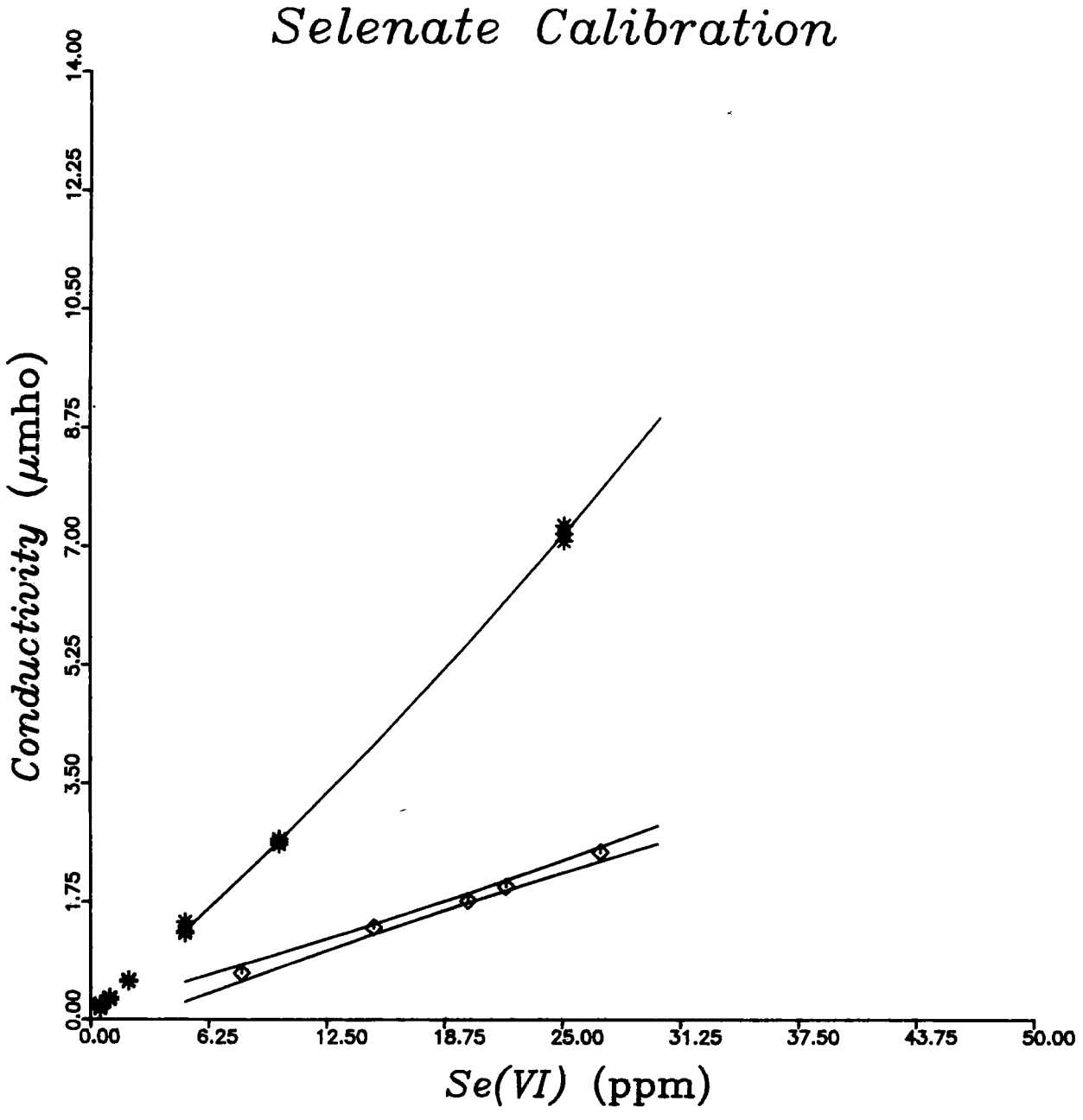


Figure 4. Calibrations for selenium (VI).

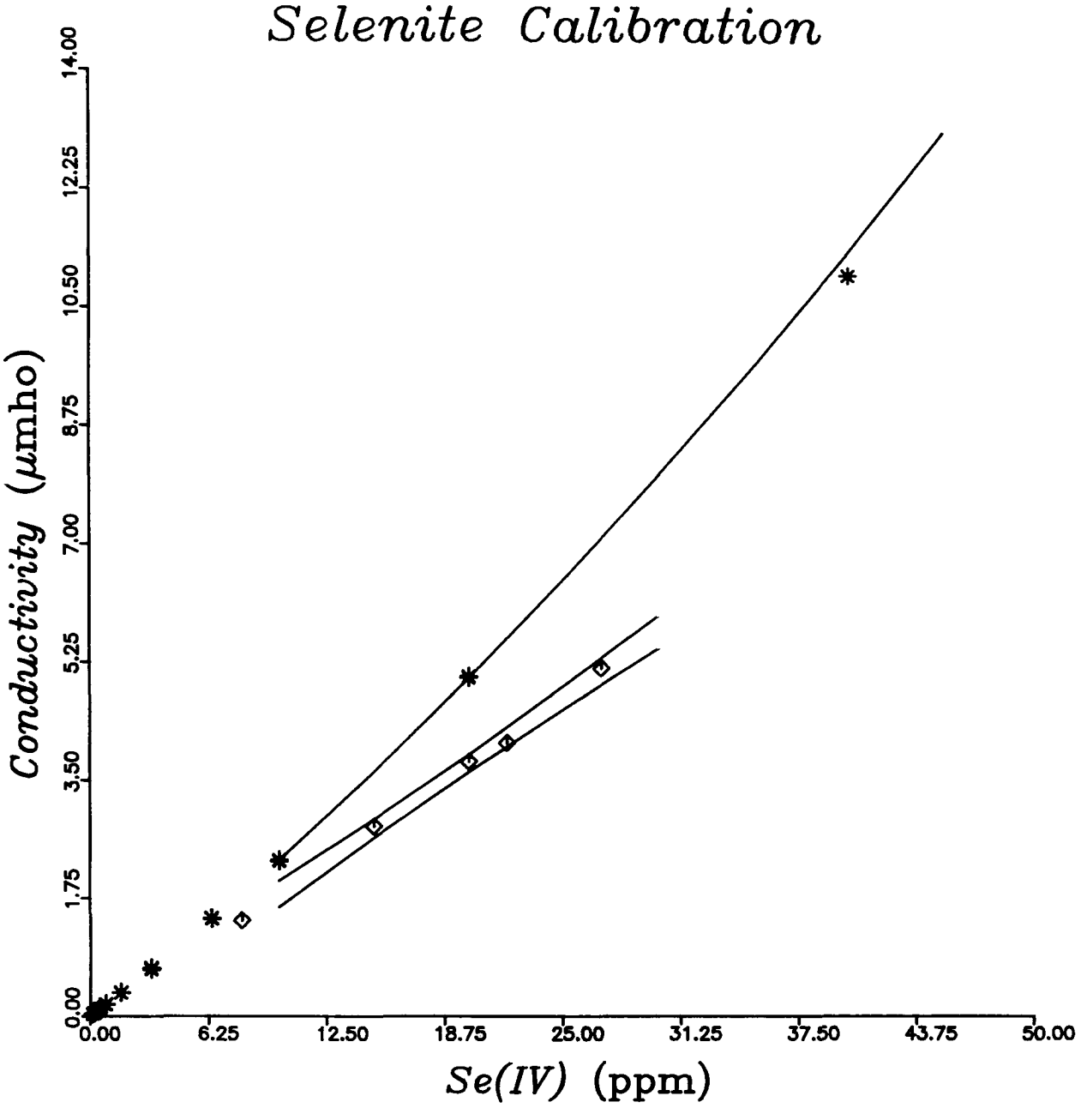


Figure 5. Calibrations for selenium (IV) by direct injection.

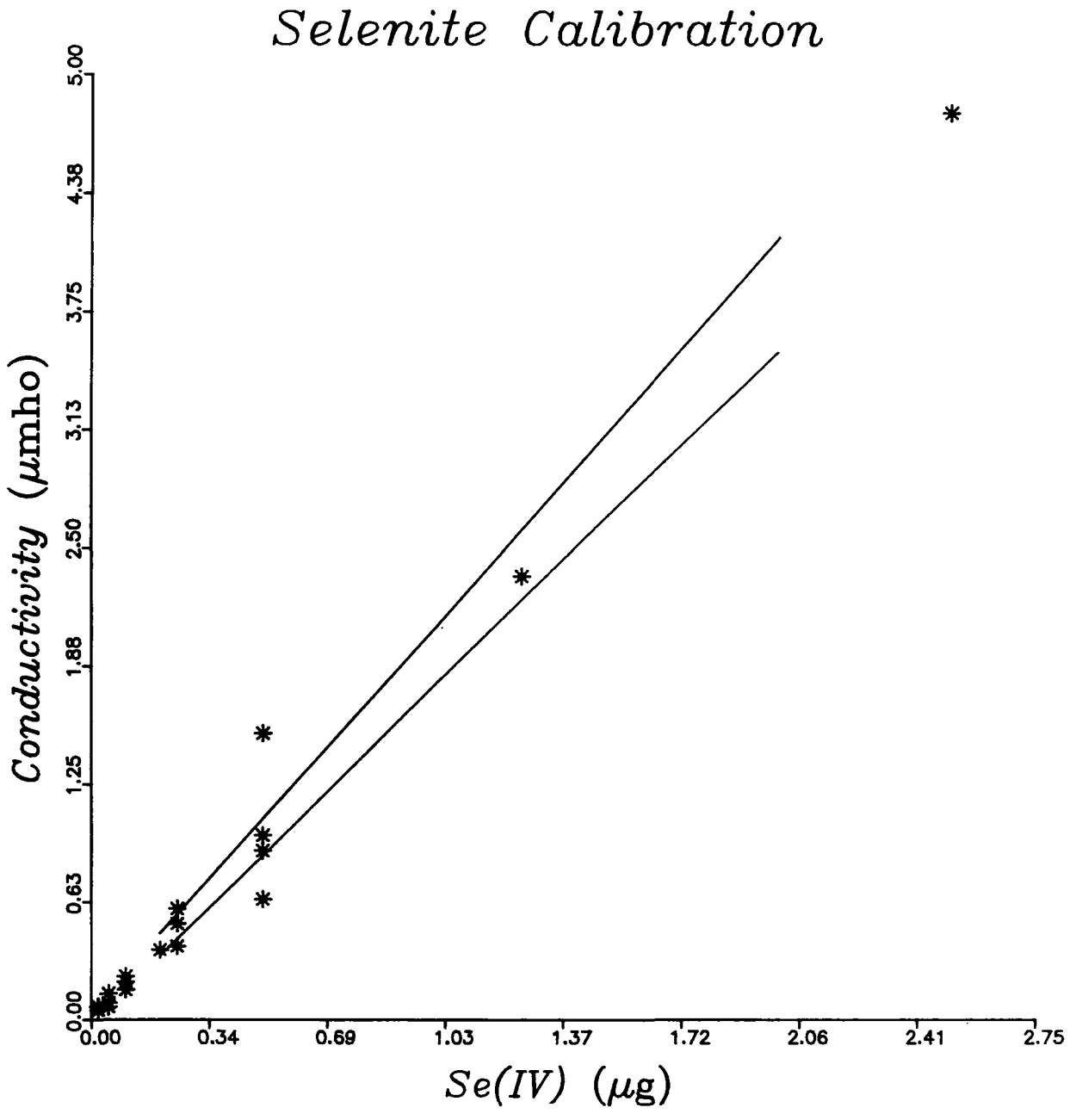


Figure 6. Calibration for selenium (IV) by concentrator column.

TABLE 1. EFFECT OF pH ON RETENTION TIME OF PROTONATED SPECIES OF ORTHOPHOSPHATE

pH	E(m$\underline{M}$)	A^{-2}	A^{-3}	Retention Time		
				Calc.	Meas.	Diff.
11.5	6.00	0.6	10.1	10.7	15.7	5.0
11.5	1.50	2.4	81.1	83.5	83	-0.5
(11.2	3.10	1.2	14.9	16.2	33.6	17.4)
9.9	2.55	1.6	1.1	2.7	10	7.3
9.7	2.29	1.8	0.8	2.6	4.6	2.0
9.6	0.73	5.6	3.0	8.6	8.4	-0.2
9.6	0.39	10.4	9.1	19.5	17.6	-1.9
9.4	1.00	4.1	.2	5.3	6.6	1.3

$C_2 = (4.1 \pm 1.4) \times 10^{-3}$
$C_3 = (4.04 \pm 0.22) \times 10^{-2}$

TABLE 2. EFFECT OF pH ON RETENTION TIME OF PROTONATED SPECIES OF ARSENATE

pH	E(m$\underline{M}$)	A^{-2}	A^{-3}	Retention Time		
				Calc.	Meas.	Diff.
11.5	6.00	0.2	13.7	13.8	9.9	-3.9
11.3	3.93	0.1	7.7	7.8	14	6.2
11.2	3.10	0.4	20.1	20.5	23	2.5
11.2	3.10	0.4	20.1	20.5	18.6	-1.9
10.0	1.94	0.4	1.6	2.0	3.5	1.5
9.7	2.29	0.5	1.1	1.6	2.6	1.0
9.6	0.73	1.6	4.1	5.7	4.4	-1.3
9.4	1.00	1.2	1.6	2.8	3.4	0.6

$C_2 = (8 \pm 14) \times 10^{-4}$
$C_3 = (4.9 \pm 0.5) \times 10^{-3}$

TABLE 4. ARSENATE CALIBRATION

0.1 mL injection, 150-mm Precolumn + 150-mm Anion Separator.
Eluent: 3 mM Na_2CO_3, 3 mM $NaHCO_3$, pH 10.0.
Flow: 1.25 mL/min. Retention time: 8.7 to 9.0 min.

Range Full-Scale μmho/cm	As(V) Concentration (ppm)	Peak Height (μmho/cm)
1	1	0.19
1	1	.20
1	2	.35
1	2	.35
1	2	.38
1	4	.79
1	4	.80
1	4	.82
3	8	1.57
3	8	1.61
3	12	2.52
10	16	3.39
10	16	3.39
10	16	3.50
10	20	4.25
10	25	5.51
10	30	6.77

$$H(\mu mho/cm) = (-0.108 \pm 0.029) + (0.2236 \pm 0.0022)\ C\ (ppm)$$

TABLE 5. BROMIDE CALIBRATION

0.1 mL injection, 500-mm Anion Separator
Standard Eluent, Flow 2.56 mL/min.

Range Full-Scale µmho/cm	Bromide Concentration (ppm)	Peak Height (µmho/cm)
1	1	0.10
1	2	.20
1	3	.33
1	4	.43
3	1	.11
3	2	.21
3	4	.44
3	8	1.00
3	16	2.09
10	8	.83
10	16	1.83
10	32	3.90
10	64	8.07
30	16	1.71
30	32	3.84
30	64	7.85
30	128	15.83
30	200	25.69

$$H(\mu mho/cm) = (-0.118 \pm 0.046) + (0.1274 \pm 0.0007)\ C\ (ppm)$$

TABLE 6. CHLORIDE CALIBRATION

0.1 mL injection, 500 mm Anion Separator,
Flow 2.56 mL/min, Std. Eluent

Range Full-Scale µmho/cm	Chloride Concentration (ppm)	Peak Height (µmho/cm)
1	0.01	0.126
1	.02	.185
1	.03	.242
1	.04	.323
1	.05	.435
3	.04	.378
3	.10	.880
3	.16	1.470
3	.24	2.285
10	.16	1.319
10	.24	1.929
10	.32	2.657
10	.40	3.366
30	.32	2.480
30	.4	3.189
30	.8	6.732

$H(\mu mho/cm) = (0.024 \pm 0.039) + (8.29 \pm 0.13)\ C\ (ppm)$

TABLE 7. NITRATE CALIBRATION

3 x 50 mm Concentrator Column, 500 mm Anion Separator
Standard Eluent; Flow 2.56 mL/min.

Range Full-Scale (μmho/cm)	Volume (mL)	Nitrate (μg)	Peak[1] Height (μmho/cm)	Range Full-Scale (μmho/cm)	Volume (mL)	Nitrate (μg)	Peak Height (μmho/cm)
30	5	5.0	5.42	3	20	0.2	0.59
10	5	5.0	5.48	3	9	0.09	0.21
10	10	2.0	2.28	3	10	0.1	0.41
10	10	5.0	5.71	3	10	0.4	0.91
10	10	1.0	1.46	3	10	0.1	0.26
30	10	6.0	7.24	3	10	0.1	0.25
10	10	6.0	7.32	3	10	0.1	0.26
10	10	0.1	0.02	3	20	0.2	0.60
10	10	0.2	0.28	3	15	0.15	0.38
10	10	0.4	0.79	3	15	0.15	0.37
10	10	0.8	1.04	1	30	0.03	0.35
10	10	1.0	1.54	1	15	0.015	0.18
3	10	1.0	1.57	1	10	0.01	0.09
3	10	0.1	0.40	1	40	0.04	0.39
				1	40	0.02	0.10
				1	20	0.01	0.02
				1	40	0.004	0.18

$$H(\mu mho/cm) = (0.207 \pm 0.040) + (1.124 \pm 0.018)\ C\ (\mu g)$$

(1) Peak heights corrected for water blank. See text.

TABLE 8. NITRITE CALIBRATION

3 x 50 mm Concentrator Column, 500 mm Anion Separator, Standard Eluent, Flow 2.56 mL/min.

Range Full-Scale µmho/cm	Volume (mL)	Nitrite Ion Injected (µg)	Peak Height* (µmho/cm)
30	25	4.0	31.00
30	20	3.2	24.71
30	20	3.2	25.47
30	15	2.4	15.74
30	15	2.4	17.83
30	15	2.4	18.07
30	10	1.6	11.25
30	10	1.6	10.67
30	5	0.8	6.58
30	5	0.8	4.69
10	20	0.96	5.99
10	15	0.72	4.28
10	10	0.48	4.28
3	20	0.32	5.2
3	20	0.32	2.38
3	15	0.24	4.54
3	10	0.16	2.96
3	10	0.16	1.22
3	5	0.08	1.22
3	5	0.08	0.60
1	20	0.13	1.8
1	20	0.13	2.0
1	20	0.16	1.8
1	20	0.13	1.7
1	15	0.10	1.5
1	10	0.06	1.2
1	10	0.06	1.40
1	5	0.03	.76

* Sum of two peaks, assuming the first is nitrate resulting from oxidation on the suppressor column.

$$H(\mu mho/cm) = (0.57 \pm 0.28) + (7.29 \pm 0.19)\ C\ (\mu g)$$

TABLE 9. PHOSPHATE CALIBRATION

3 x 50 mm Concentrator Column, 500 mm Anion Separator.
Standard Eluent, Flow 2.56 mL/min.

Range Full-Scale µmho/cm	Volume (mL)	Phosphate Ion Injected (µg)	Peak Height (µmho/cm)
1	5	0.05	0.07
1	10	0.10	0.14
1	15	0.15	0.22
1	20	0.20	0.26
1	5	0.05	0.06
1	10	0.10	0.12
1	15	0.15	0.19
1	25	0.25	0.28
3	5	0.15	0.18
3	15	0.45	0.67
3	10	0.30	0.45
3	25	0.75	1.15
3	20	0.60	0.90
10	5	1.5	2.09
10	10	3.0	4.86
10	5	0.5	0.63
10	10	1.0	1.46
10	15	1.5	2.28
10	20	2.0	3.23
10	25	2.5	4.17

$$H(\mu mho/cm) = (-0.017 \pm 0.029) + (1.406 \pm 0.071)\ \mu g + (0.084 \pm 0.025)\ (\mu g)^2$$

TABLE 10. SELENATE CALIBRATION

0.1 mL injection, Precolumn plus 500-mm Anion Separator; Standard Eluent; Flow 2.56 mL/min.

Range Full-Scale µmho/cm	Se(VI) Concentration (ppm)	Peak Height (µmho/cm)
3	8	0.69
3	15	1.37
3	20	1.77
3	22	1.98
3	27	2.49

$$H(\mu mho/cm) = (-0.058 \pm 0.045) + (0.0934 \pm 0.0023)\ C\ (ppm)$$

TABLE 11. SELENATE CALIBRATION

0.1 mL injection, 150-mm Precolumn plus 150-mm Anion Separator
Eluent: 1 mM Na_2CO_3, 10 mM $NaHCO_3$, pH 9.75
Flow: 1.25 mL/min; Retention time: 14.7 min.

Range Full-Scale µmho/cm	Se(VI) Concentration (ppm)	Peak Height (µmho/cm)
30	25	7.09*
30	25	7.20
30	25	7.32*
10	10	2.60
10	10	2.64
10	10	2.68
3	5	1.31
3	5	1.45*
3	5	1.28
1	2	0.57
1	2	0.58
1	2	0.56
1	1	0.29
1	1	0.30
1	1	0.32
1	0.5	0.16
1	0.5	0.22
1	0.5	0.19

$$H(\mu mho/cm) = (0.072 \pm 0.010) + 0.2376 \pm 0.0030)\ C + (0.0019 \pm 0.0012)\ C^2$$

* Outliers omitted (> 2 standard deviations)

TABLE 12. SELENITE CALIBRATION

0.1 mL injection, 3 x 150-mm Precolumn plus 500-mm Anion Separator.
Standard Eluent, Flow 2.56 mL/min.

17 Jan 79 Retention time 5.9 min			12 June 1979 Retention time 7.4 min		
Range Full-Scale µmho/cm	Se(IV) Concentration (ppm)	Peak Height (µmho/cm)	Range Full-Scale µmho/cm	Se(IV) Concentration (ppm)	Peak Height (µmho/cm)
1	0.1	0.03	3	8.0	1.42
1	.2	.04	10	15.0	2.82
1	.3	.07	10	20.0	3.78
1	.4	.09	10	22.0	4.06
1	.5	.11	10	27.0	5.16
1	.8	.18			
1	1.6	.35	H(µmho/cm) =	(-3.2 ± 2.1) +	
1	3.2	.71		(4.93 ± 0.22) C (ppm)	
3	.8	.17			
3	1.6	.35			
3	3.2	.71			
3	6.4	1.45			
10	3.2	.69			
10	6.4	1.44			
10	10.0	2.32			
10	20.0	5.04			
30	10.0	2.30			
30	20.0	5.02			
30	40.0	10.98			

$$H(\mu mho/cm) = 0.0088 + 0.2069\ C + 0.00272\ C^2 - 0.000026\ C^3$$

TABLE 13. SELENITE CALIBRATION

3 x 50 mm Concentrator Column, 150-mm Precolumn and 500-mm Anion Separator. Standard Eluent, Flow 2.56 mL/min.

Range Full-Scale µmho/cm	Volume (mL)	Se(IV) Ion Injected (µg)	Peak Height (µmho/cm)
1	25	0.05	.09
1	50	.10	.23
1	5	.05	.07
1	10	.10	.16
1	25	.25	.39
1	10	.02	.05
1	5	.10	.20
1	10	.20	.37
3	25	.50	.90
3	5	.25	.51
3	10	.50	.98
3	25	1.25	2.56
1	50	.10	.16
1	10	.02	.07
1	25	.05	.14
3	25	1.25	2.35
3	10	.50	.64
10	50	2.50	4.80
3	50	.50	1.52
1	25	.25	.59

$$H(\mu mho/cm) = (0.014 \pm 0.044) + (1.932 \pm 0.061)\ C\ (\mu g)$$

TABLE 14. SULFATE CALIBRATION

0.1 mL injection, 500-mm Anion Separator,
Standard Eluent, Flow 2.56 mL/min.

Range Full-Scale µmho/cm	Sulfate Concentration (ppm)	Peak Height (µmho/cm)
1	1	.10
1	2	.22
1	4	.42
3	2	.18
3	4	.42
3	8	.87
3	12	1.38
10	8	.85
10	12	1.34
10	16	1.89
10	20	2.36
30	16	1.71
30	20	2.24
30	50	6.38
30	100	13.82
30	100	14.06
30	150	20.26

$H(\mu mho/cm) = (-0.247 \pm 0.066) + (0.1384 \pm 0.0013)\ C\ (ppm)$

TABLE 15. RETENTION TIMES AND DETECTION LIMITS OF ANIONS

Eluent: 2.4 mM Na_2CO_3 plus 3 mM $NaHCO_3$
Flow: 2.56 mL/min.
3 x 500-mm Anion Separator Column

Ion	Retention Time (Min.)	Detection Limit (µg)
Cl	3.5	0.002
NO_2	4.5-5.0	0.15 *
SeO_3	5.9	0.10 *
		.008
PO_4	7.0-7.6	0.07 *
Br	9.5	0.15
NO_3	11.1	0.14 *
SO_4	15.5-16.7	0.20
SeO_4	29.2	0.011

* Determined on concentrator column; others, by direct injection of 0.1 mL.

REFERENCES

1. Hoover, T. B. Inorganic Species in Water: Ecological Significance and Analytical Needs. EPA-600/3-78-064. U.S. Environmental Protection Agency, Athens, GA (July 1978). 108 pp.

2. Sawicki, E. Potential of Ion Chromatography. In: Ion Chromatographic Analysis of Environmental Pollutants, E. Sawicki, J. D. Mulik, and E. Wittgenstein, eds. Ann Arbor Science Publishers, Ann Arbor, MI (1978). pp. 1-9.

3. Ion Chromatographic Analysis of Environmental Pollutants. Vol. 1. Sawicki, E., J. D. Mulik, and E. Wittgenstein (eds.). Ann Arbor Science Publishers, Ann Arbor, MI (1978). 210 pp.

4. Mulik, J. D. and E. Sawicki. Ion Chromatography. Environ. Sci. Technol. 13 (7), 804-809 (1979).

5. Small, H., T. S. Stevens, and W. C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Detection. Anal. Chem. 47(11), 1801-1809 (Sept. 1975).

6. Kolthoff, I. M. and R. Belcher. Volumetric Analysis. Vol. 3. Titration Methods: Oxidation-Reduction Reactions. Interscience Publishers, New York (1957). p. 70.

7. Rieman, W. and H. F. Walton. Ion Exchange in Analytical Chemistry. Pergamon Press, Oxford (1970). p. 100.

8. Colaruotolo, J. F. Organic Elemental Microanalysis by Ion Chromatography. In: Ion Chromatographic Analysis of Environmental Pollutants, E. Sawicki, J. D. Mulik, and E. Wittgenstein, (eds.). Ann Arbor Science Publishers, Ann Arbor, MI (1978). pp. 149-167.

9. Lathouse, J. and R. W. Coutant. Determination of Anions in Filter Catch Samples. In: Ion Chromatographic Analysis of Environmental Pollutants, E. Sawicki, J. D. Mulik, and E. Wittgenstein, (eds.). Ann Arbor Science Publishers, Ann Arbor, MI (1978). pp. 53-64.

10. Wetzel, R. A., C. L. Anderson, H. Schleicher, and G. D. Cook. Determination of Trace Level Ions by Ion Chromatography with Concentrator Columns. Anal. Chem. 51(9), 1532-1535 (Aug. 1979).

11. Natrella, M. G. Experimental Statistics. National Bureau of Standards Handbook 91. U.S. Department of Commerce, Washington, DC (1963). 5.18.

12. Hansen, L. D., B. E. Richter, D. K. Rollins, J. D. Lamb, and D. J. Eatough. Determination of Arsenic and Sulfur Species in Environmental Samples by Ion Chromatography. Anal. Chem. 51(6), 633-637 (May 1979).

13. Koch, W. F. Complication in the Determination of Nitrite by Ion Chromatography. Anal. Chem. 51(9), 1571-1573 (August 1979).

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-80-020		

4. TITLE AND SUBTITLE	5. REPORT DATE
Ion Chromatography of Anions	March 1980 issuing date
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Thomas B. Hoover and George D. Yager	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory U.S. Environmental Protection Agency Athens, Georgia 30605	A37B1D
	11. CONTRACT/GRANT NO. In-house

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Research Laboratory-Athens, GA Office of Research and Development U.S. Environmental Protection Agency Athens, Georgia 30605	Interim, 7/78-7/79
	14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A Dionex Model 10 Ion Chromatograph was evaluated for the measurement of anionic species in water. The theoretical effect of hydrogen ion activity (pH) on the elution time of phosphate and arsenate was tested and empirical selectivity coefficients were determined for the major protolytic species of these acids. Calibration curves were obtained for arsenate, bromide, chloride, nitrate, nitrite, phosphate, selenate, selenite, and sulfate by direct injection of 0.1 mL of standards and, in most cases, by preconcentration of 5 to 50 mL of solution on the ion exchange concentrator columns available from the instrument manufacturer. Detection limits for ions other than chloride were approximately 0.2 µg independent of the method of sample introduction. For chloride the detection limit was 2 ng, by direct injection. The concentrator column permitted determination of any of the above ions at concentrations greater than 10 µg/L.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chemical analysis Water analysis Anions Concentrators	Ion chromatography	07B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	41
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

* U.S. GOVERNMENT PRINTING OFFICE: 1980-657-146/5625