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CHARACTERIZATION OF INDIRECT PHOTOMETRY FOR THE DETERMINATION OF INORGANIC ANIONS IN NATURAL WATER BY ION CHROMATOGRAPHY

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SUMMARY

A high-performance liquid chromatographic method based on indirect photometric detection is described for the analysis of inorganic anions in natural waters. Up to ten anions can be analyzed simultaneously with detection limits at the nanogram level. The working range covers three decades in concentration and the short term stability is around 1% for most anions. The validity of the method is proven by an inter-laboratory study and by the analysis of certified samples. The main advantages of this method over ion chromatography with suppressed conductivity detection are its simple response standardization and its simplicity as it involves conventional high-performance liquid chromatography equipment.

INTRODUCTION

The determination of inorganic anions in natural water is becoming increasingly important as it allows a better understanding of environmental pollution. The standard methods used are usually based on a specific reaction for each species (*e.g.*, colorimetric or electrochemical reactions¹). When a large number of determinations are required, the application of specific reactions for anions becomes time consuming and the possibility of the simultaneous separation, identification and quantification of several anions is then of interest. Ion chromatography with suppressed conductivity detection is one of the most popular methods that satisfy these objectives². However, the technique involves chromatographic equipment that is very specific to the determination of ionic species, such as a suppression column, an ionic separation column and a conductivity detector. Also, as conductivity is sensitive to temperature, a temperature controller is often needed. Recently, efforts have been made to avoid the use of a suppression column, as it introduces an additional dead volume and needs special care such as periodic regeneration. The use of a low-conductivity eluent was found to allow omission of the suppression column^{3,4}, but it still requires the use of a specific detector.

In this paper, an indirect photometric chromatographic method with an ultra-

violet detector is described for the determination of inorganic anions. Although the theoretical aspects of the technique are now well known⁵, its application to the analysis of real samples has not been widely reported. The purpose of this work was to characterize the method in terms of sensitivity, detection limits, working range and stability in order to define its possibilities and limitations for the determination of several important inorganic anions. The analysis of natural waters was also investigated and the validity of the method was established by inter-laboratory studies and by comparison with quality control samples.

EXPERIMENTAL

Instrumentation

The liquid chromatograph used consisted of a Waters Assoc. (Bedford, MA, U.S.A.) Model 510 pump and a Model 481 variable-wavelength UV detector. A Model 7125 six-port high-pressure switching injection valve (Rheodyne, Cotati, CA, U.S.A.) was used with a 500- μ l injection loop. A Waters IC Pak (25 μ m) guard column (0.5 cm \times 0.6 cm I.D.) was inserted before the separation column (15 cm \times 0.4 cm I.D.) which was packed with PRPX-100 polystyrene-divinylbenzene anion exchanger (10 μ m, 200 μ equiv./g) (Hamilton, Reno, NV, U.S.A.).

Data acquisition was performed with an integrator (Shimadzu, Kyoto, Japan) or via a digital voltmeter connected with an IEEE-488 card (Capital Equipment, Burlington, NY, U.S.A.) to a IBM-XT microcomputer. In this instance Nelson Analytical (Cupertino, CA, U.S.A.) (3000 series chromatographic data system) was used for peak processing.

Reagents and procedures

The water used for the preparation of the various solutions was distilled and passed through a Millipore (Bedford, MA, U.S.A.) Milli-Q purification system. Standard solutions (1000 mg/l) of fluoride, nitrite, chloride, nitrate, bromide, phosphate, sulfate, iodide, propionate, acetate, formate and carbonate were prepared by dissolving appropriate amounts of analytical-reagent grade sodium or potassium salts in pure water. These solutions were kept in polypropylene bottles and were diluted daily to give the multi-anion solutions required. Prior to the analysis, the solutions were filtered through a 0.45- μ m filter (25-mm HAWP or HVLP filter; Millipore).

The eluents were prepared daily from 0.1 M potassium hydrogenphthalate solution prepared from the analytical-reagent grade salt. The pH of the mobile phase was adjusted with 0.1 M sodium hydroxide solution. The mobile phases were filtered through a 0.45- μ m filter (47-mm HAWP or HVLP) and degassed in a ultrasonic bath before use.

Samples

Samples of natural water (river or lake) were kept at 4°C in polypropylene bottles before and after analysis.

RESULTS AND DISCUSSION

Practical considerations

Selectivity. Various analytical methods have been used to determine the most important inorganic anions in natural water, *viz.*, fluoride, chloride, nitrite, nitrate, phosphate, sulphate and iodide¹. However, in contrast to these methods, chromatography is not based on a specific reaction for each analyte but on separation. It is therefore important during the method development to consider all species likely to be present. Among the various anions, carbonate is an important anion to take into account and, based on water analyses reported by Jones and Tarter⁶, bromide could also be a potential interferent. Low-molecular-weight organic acids that could elute in a relatively short time and interfere in inorganic determinations also need to be considered. Brocco and Tappa⁷ found traces of acetic, formic and propionic acids in rain water.

All these species were taken into consideration when optimizing the chromatographic separation.

Sensitivity. In indirect photometry, the signal S produced by the UV detector when an analyte anion A^- elutes in an eluent containing E^- species is given by

$$S = l(\varepsilon_{E^-} C_{E^-} - \varepsilon_{A^-} C_{A^-})$$

were l = optical path length, ε = molar absorptivity and C = concentration. For maximum sensitivity, ε_{A^-} should be zero. Most inorganic anions are transparent above 220 nm and a higher detection wavelength should therefore be chosen.

Another important point in indirect photometry is to obtain a "background" absorbance between 0.2 and 0.8 for the eluent species at the detection wavelength in order to minimize the spectrophotometric error. An absorbance range that is steady near the detection wavelength is also needed in order to minimize the imprecision of the wavelength.

pH of the eluent. Two types of interferences are often observed in the determination of inorganic anions by indirect photometric chromatography. The first arises from carbonate, which may be present in large amounts in natural waters. The simplest way to eliminate carbonate is to use an eluent at $\text{pH} < 6$ so that the anion will be fully protonated.

The second type of interference is that resulting from the system peak, the presence of which seems to be due to the elution of neutral molecules of the eluent on injection of a water sample⁸. These molecules are believed to be retained on the chromatographic column by a reversed-phase mechanism, as about 85% of a low-capacity ion-exchange column is unfunctionalized (*i.e.*, does not have any ionized group)⁹. The retention time of this peak depends on a large number of parameters (nature and concentration of the eluent, pH of the mobile phase, presence of a modifier in the eluent, etc.). Its existence can be a real problem if it overlaps with an analyte peak or if it appears late in the chromatogram and increases the time of analysis. To avoid this peak, the eluent must be completely ionized at the pH chosen.

Optimization of the chromatographic system

Keeping all the above practical considerations in mind, the chromatographic

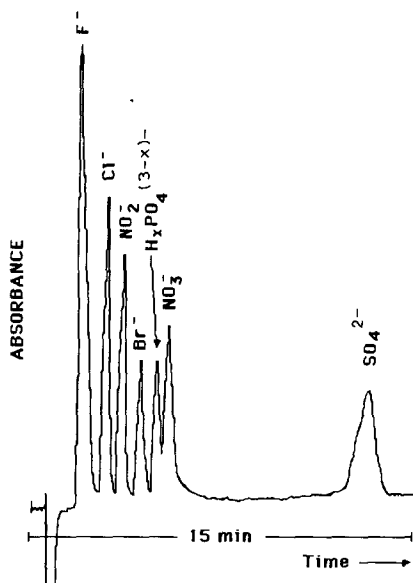


Fig. 1. Typical separation of inorganic anions by indirect photometry chromatography. For experimental conditions, see Table I.

system was optimized in terms of separation and detection. Three commonly used organic anions were considered as UV-active eluent species: *p*-hydroxybenzoate, *p*-toluenesulfonate and phthalate. The best separation conditions were found with phthalate at a concentration of 0.8 mM at pH 6.8. The detection wavelength was set at 265 nm. A typical separation obtained under these conditions is shown in Fig. 1. The separation with *p*-toluenesulfonate could not be easily optimized and good detection with *p*-hydroxybenzoate in the eluent could not be obtained.

The only anion of interest that could not be determined using these conditions was iodide, as its elution time was too long. It was observed that carbonate, formate and acetate, if present at low concentrations, would not interfere with any determination as they elute between fluoride and chloride (Fig. 2). Propionate was found to co-elute with bromide but probability of finding both species in natural water is low. If a peak appears at the elution time of bromide or propionate, it would always be possible to modify the pH of the mobile phase slightly so that the degree of ionization of the propionic acid would change and the propionate would elute at a different time. Interference from the system peak was avoided because at this pH, phthalate is fully ionized. The optimum conditions are reported in Table I.

Analytical performances

Sensitivity. An interesting point in indirect photometry is the standardization of a UV-transparent solute response. In fact, if we consider the elution of an analyte, this species will displace an equivalent concentration of a UV-active eluent species as required by electroneutrality. The sensitivity, in terms of peak area per unit concentration expressed in normality, is then independent of the nature of the analyte. This behavior was studied and the results obtained were 730, 700, 750 and 750 mV s/mN

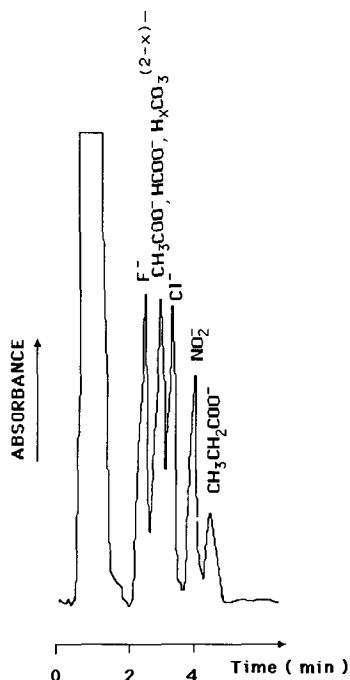


Fig. 2. Retention of organic anions potentially present in natural waters. For experimental conditions, see Table I.

for Cl^- , NO_2^- , Br^- and NO_3^- , respectively. From these results, it was clear that the response of a known solute could be used to evaluate the concentration of other unknown analytes with an accuracy of $\pm 10\%$ without the need to calibrate for each species.

Detection limits. The detection limits, DL , were evaluated according to Foley and Dorsey¹⁰, i.e., $DL = 3\sigma_b/4$, where σ_b is the noise-to-signal ratio. The results obtained are given in Table II and are compared with those reported by the U.S. Environmental Protection Agency (EPA) in their test method using ion chromatography with suppressed conductivity detection².

The results indicate that indirect photometry is comparable to ion suppressed conductivity as far as the detection limits are concerned.

TABLE I
OPTIMUM CONDITIONS FOR THE SEPARATION OF INORGANIC ANIONS

Operation	Parameter	Value
Separation	Phthalate concentration (mM)	0.8
	pH	6.8
	Flow-rate (ml/min)	1.2
	Injection volume (μl)	500
Detection	Wavelength (nm)	265
	Response time (s)	1

TABLE II
DETECTION LIMITS FOR INORGANIC ANIONS

Anion	Detection limit (ng)	
	Indirect photometry ^a	Conductivity with suppression ^b
F ⁻	1	1
Cl ⁻	1	1
NO ₂ ⁻	3	1
NO ₃ ⁻	4	6
H _x PO ₄ ^{(3-x)-}	21	18
SO ₄ ²⁻	4	20

^a The volume injected was 500 μ l.

^b The volume injected was 100 μ l. The experimental conditions were as described in the test method approved by the EPA for the determination of inorganic anions in water by ion chromatography: chromatographic system, Dionex; eluent, 0.003 M NaHCO₃-0.0024 M Na₂CO₃; regeneration solution, 0.0125 M H₂SO₄.

Short-term stability. The short-time stability was evaluated from the results obtained with five injections of a multi-anion solution at ca. 2 mg/l of each species. Table III gives the results obtained at a 95% confidence level.

The short-time stability was acceptable for most anions. The poorest results were obtained for nitrate and phosphate, and can be explained by the small difference between their elution times. As the separation was optimized assuming bromide could be present, the composition of the mobile phase was chosen so that phosphate would elute between nitrate and bromide. As bromide is uncommon in natural waters, once its absence has been confirmed it is possible to modify the composition of the mobile phase slightly to improve the separation of phosphate and nitrate, and this would result in better quantification.

Working range. For the analysis of a multi-anion solution, it was found that the maximum concentration or amount that could be injected was limited by saturation of the capacity of the column, resulting in poor peak shapes. The term "working range" is then more appropriate than "linear range".

TABLE III
SHORT-TERM STABILITY AND WORKING RANGE

Anion	Short-term stability (%) ^a	Upper limit (μ g)
F ⁻	1.0	2
Cl ⁻	2.8	2
NO ₂ ⁻	0.5	2
NO ₃ ⁻	3.5	2.5
H _x PO ₄ ^{(3-x)-}	5.0	4
SO ₄ ²⁻	2.7	1.5

^a The results are reported as a 95% confidence level and were evaluated with five measurements.

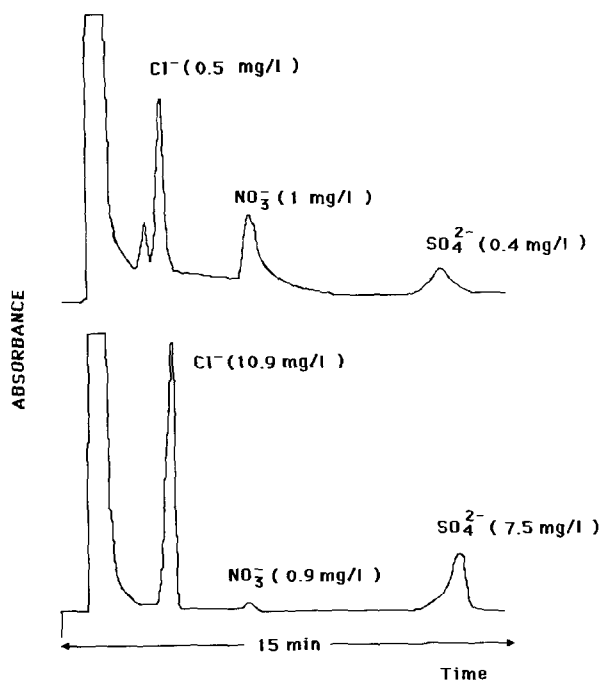


Fig. 3. Analysis of lake water by indirect photometry chromatography. For experimental conditions, see Table I.

In Table III the maximum amounts of a multi-anion solution that could be injected on to the chromatographic column are reported. It is important to note that if resolution is not affected by the peak shape, higher concentrations could be injected as the relationship between peak area and concentration is linear over these limits.

Analysis of natural water

In order to examine the suitability of the method for the determination of inorganic anions, several types of natural water were analysed, an inter-laboratory study was conducted and certified samples were analysed.

Examples of chromatograms obtained for lake and river water samples are illustrated in Fig. 3. As expected, when a large amount of hydrogencarbonate was present in the sample, it interfered with the chloride determination (Fig. 4). Decreasing the pH of the mobile phase could prevent the ionization of the hydrogencarbonate. In these particular instances, the analysis needs to be repeated. First an analysis was made using the optimum conditions for separation and then a second separation at lower pH was performed to eliminate the carbonate interference. The interference from hydrogencarbonate is a disadvantage in our method and in the EPA method by ion chromatography with suppressed conductivity detection.

In order to evaluate the accuracy of the method, an inter-laboratory study was undertaken. Nine lake water samples were analysed by 46 laboratories (university, industrial, government and private laboratories) and the results were compared. In most instances the determinations were done by ion chromatography with suppressed

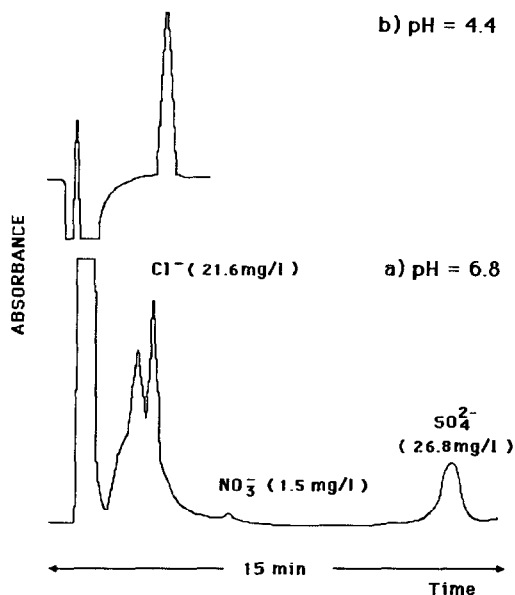


Fig. 4. Analysis of river water by indirect photometry chromatography. (a) For experimental conditions, see Table I. (b) The carbonate interference was removed by decreasing the pH of the mobile phase from 6.8 to 4.4.

TABLE IV

INTER-LABORATORY RESULTS

Sample No.	Anion ^a	Concentration (mg/l)		Standard deviation (mg/l) ^b	Confidence interval (95%) (mg/l)
		Median	Obtained		
1	Cl ⁻	0.495	0.5040	0.0006	0.501–0.506
	NO ₂ ⁻ /NO ₃ ⁻ /N	0.210	0.217	0.007	0.19–0.25
	SO ₄ ²⁻	0.360	0.37	0.01	0.33–0.41
2	Cl ⁻	0.765	0.432	0.003	0.42–0.44
	NO ₂ ⁻ /NO ₃ ⁻ /N	0.067	0.058	0.002	0.049–0.067
	SO ₄ ²⁻	1.01	0.61	0.01	0.57–0.65
3	Cl ⁻	0.865	0.45	0.03	0.3–0.6
	NO ₂ ⁻ /NO ₃ ⁻ /N	0.106	0.096	0.002	0.087–0.105
	SO ₄ ²⁻	3.10	2.95	0.07	2.6–3.2
4	Cl ⁻	10.9	10.6	0.2	9.7–11.5
	NO ₂ ⁻ /NO ₃ ⁻ /N	0.223	0.164	0.006	0.14–0.19
	SO ₄ ²⁻	7.49	7.7	0.1	7.3–8.1
5	Cl ⁻	0.543	0.553	0.009	0.51–0.59
	NO ₂ ⁻ /NO ₃ ⁻ /N	0.17	0.14	0.01	0.10–0.18
	SO ₄ ²⁻	4.87	4.70	0.07	4.4–5.0
7	Cl ⁻	4.66	4.135	0.004	4.12–4.15
	NO ₂ ⁻ /NO ₃ ⁻ /N	0.066	0.072	0.003	0.06–0.08
	SO ₄ ²⁻	5.95	6.0	0.1	5.6–6.4
9	Cl ⁻	11.6	11.3	0.1	10.9–11.7
	NO ₂ ⁻ /NO ₃ ⁻ /N	0.164	0.14	0.01	0.10–0.18
	SO ₄ ²⁻	15	14.4	0.2	13.5–15.3

^a NO₂⁻/NO₃⁻/N: the concentrations of nitrite and nitrate are expressed as nitrogen.

^b The standard deviation was obtained for three measurements.

conductivity detection using the experimental procedures recommended by the EPA. Nitrite and nitrate were often determined by other standard techniques (spectrophotometry, Technicon AutoAnalyzer, liquid chromatography). In Table IV the results of the inter-laboratory study are given and are compared with the values obtained by indirect photometric chromatography. Two major differences were observed. In general, the agreement between our results and the median is good except for chloride and sulphate in sample 2 and chloride in sample 3. These discrepancies could not be explained by contamination or by co-elution of two analytes, as the values obtained were lower than expected. It also could not be attributed to a loss of sample (leak in the injector), as all anions in the same sample did not show lower concentrations. In our laboratory, the concentrations found by external calibration were corroborated by standard additions. The discrepancies obtained could not be explained. Fortunately, all other samples analysed were found to have concentrations in the expected range.

The validity of the method was also established by the analysis of EPA certified samples. As reported in Table V, in all instances the concentrations obtained by our method were in the range of the confidence intervals given by the EPA. Only fluoride, chloride, nitrate and sulphate were detected in the natural water analysed and it was confirmed by this study of certified samples that as far as these anions are concerned good accuracy could be obtained.

CONCLUSION

The results clearly indicate that indirect photometry is comparable to ion chromatography with suppressed conductivity for the determination of inorganic anions, but has the advantages of being simpler and more versatile. The method was successfully used for the analysis of natural waters.

TABLE V
ANALYSIS OF EPA CERTIFIED SAMPLES

Anion ^a	Value ^b	True value (mg/l)	Mean recovery (mg/l)	Confidence interval (95%) (mg/l)
N-NO ₃ ⁻	C	0.14	0.14	0.11–0.17
	O		0.139	0.131–0.145
P-PO ₄ ³⁻	C	0.35	0.35	0.33–0.37
	O		0.325	0.319–0.331
F ⁻	C	2.75	2.7	2.5–3.0
	O		2.69	2.66–2.72
N-NO ₃ ⁻	C	10.30	10.2	9.5–11.0
	O		10.1	9.7–10.3
Cl ⁻	C	17.8	18.0	16.1–19.9
	O		18.0	17.2–18.8
SO ₄ ²⁻	C	7.2	7.0	5– 9
	O		7.3	7.1– 7.5

^a N-NO₃⁻: The concentration of nitrate is expressed as nitrogen. P-PO₄³⁻: The concentration of phosphate is expressed as phosphorus.

^b C = certified; O = obtained.

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