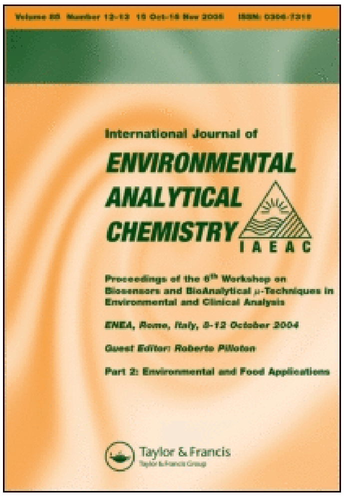

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Guillot, Isabel and Guardino, Xavier(1986) 'Single Column Ion Chromatographic Determination of Inorganic Acids in Workroom Places', International Journal of Environmental Analytical Chemistry, 24: 1, 75 — 84
To link to this Article: DOI: 10.1080/03067318608076460
URL: http://dx.doi.org/10.1080/03067318608076460

Intern. J. Environ. Anal. Chem., 1986, Vol. 24, pp. 75–84
0306-7319/86/2401-0075 $18.50/0

Printed in Great Britain

Single Column Ion Chromatographic Determination of Inorganic Acids in Workroom Places

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(*Received June 19, 1985; in final form August 30, 1985*)

Single Column Ion Chromatography (SCIC) combines low capacity-columns, low conductivity eluents and a detector with considerable electronic supression capability and enables quantitation of ions at the ppm level without the need of a suppressor column associated with other forms of Ion Chromatography.

Vapors and aerosols of inorganic acids are collected on filter and silica gel tubes and analyzed directly by SCIC. A conventional liquid chromatograph with a low capacity column and a conductimetric detector is used to analyze aerosols of Cl^-, Br^-, NO_3^- and $SO_4^=$ with good results.

KEY WORDS: Single Column Ion Chromatography (SCIC), inorganic acids, workroom places.

INTRODUCTION

In recent years there has been a growing need for reliable methods for the analysis of mixtures of common anions both in environmental samples and in dilute aqueous solutions. Such an approach has not been available until a technique developed by Small and coworkers[1] and called "Ion Chromatography" was published. This system uses two columns; in the first one the separation step occurs and the function of the second is to remove most of the background conductance of the eluent.

This instrument, called Ion Chromatograph, allows good resolution of many ion mixtures with high sensitivity, and it has been used in many applications, especially in the analysis of environmental samples. There are two major drawbacks: The eluent has to be a base and the suppressor column must be regenerated periodically to remove unwanted ions. This is not the case if hollow fiber suppressors are used,[2-4] but in that case resolution loss occurs.

In the last years, a number of new developments have increased the versatility of ion chromatography. In this sense, Fritz, Smuckler and co-workers[5-7] have introduced a single column method called Single Column Ion Chromatography. The combination of low capacity columns, low conductivity eluents and a detector with considerable electronic suppression capability avoids the suppressor column enabling the quantification of ions at the ppm level.

In spite of the fact that the Dionex(R) type ion chromatography has better sensitivity, due to the effective decrease of background conductivity by the suppressor column, the Single Column Ion Chromatography presents some advantages. First the elimination of one column constitutes itself an advantage and besides the regeneration procedure is avoided.

On the other hand, there is also a great economical advantage, since it is not necessary to buy an ion chromatograph. Good results can be obtained by connecting a conductivity detector and a low capacity column to a conventional high resolution liquid chromatograph. There is also the possibility of using different detectors as electrochemical and U.V. detector.[8,9] This offers two possibilities: direct reading or indirect reading, the latter also called Indirect Photometric Chromatography.

For these reasons, Single Column Ion Chromatography is finding increasing applications in environmental and industrial hygiene chemistry.

Industrial hygiene often requires the determination of vapor and aerosol concentrations in air. The most common determination procedure has been the sampling with filters and absorber solutions followed by conventional analytical techniques.[10-12]

In this sense, filters and silica gel tubes are used for collection and determination of inorganic acids. Moreover, the samples can be desorbed with the same solvent as used for chromatographic separation and analyzed directly by Single Column Ion Chromatography.

This work describes the application of Single Column Ion Chromatography with conductivity detector for the determination of sulfuric and nitric acid, and of hydrogen chloride and hydrogen bromide in air.

EXPERIMENTAL

Apparatus

A HPLC system (Waters Assoc., Milford, MA. U.S.A.) equipped with a Conductimetric Detector (Wescan Instruments, Inc. U.S.A.), a Model U6K injector, a Model 6000 A solvent delivery pump and a Wescan Anion low capacity column (250 × 4.6 mm) was used.

Chemicals

Deionized, filtered water. The water must be filtered before use to avoid plugging valves in the chromatograph.

Potassium hydrogen phtalate (KHP, analytical reagent grade).

Potassium hydroxide. Dissolve 2 or 3 pellets of KOH in 25 ml of filtered water to prepare an approx 0.1 M KOH solution.

Stock standard solutions:

Potassium chloride (1 mg Cl^-/ml). Dissolve 0.209 g KCl/100 ml eluent.

Potassium bromide (1 mg Br^-/ml). Dissolve 0.148 g KBr/100 ml eluent.

Potassium nitrate (1 mg NO_3^-/ml). Dissolve 0.163 g KNO_3/100 ml eluent.

Potassium sulfate (1 mg $SO_4^=$/ml). Dissolve 0.181 g K_2SO_4/100 ml eluent.

Eluent (4×10^{-3} M potassium hydrogen phtalate). Dissolve 0.82 grams of potassium hydrogen phtalate in 1000 ml of degassed deionized water and adjust pH to 4.5 with dilute (approx. 0.1 M) KOH solution.

Air sampling and sample preparation

Inorganic acids are collected on filters of cellulose (sulfuric acid) or silica gel tubes (Figure 1) with 500 mg in the front section and

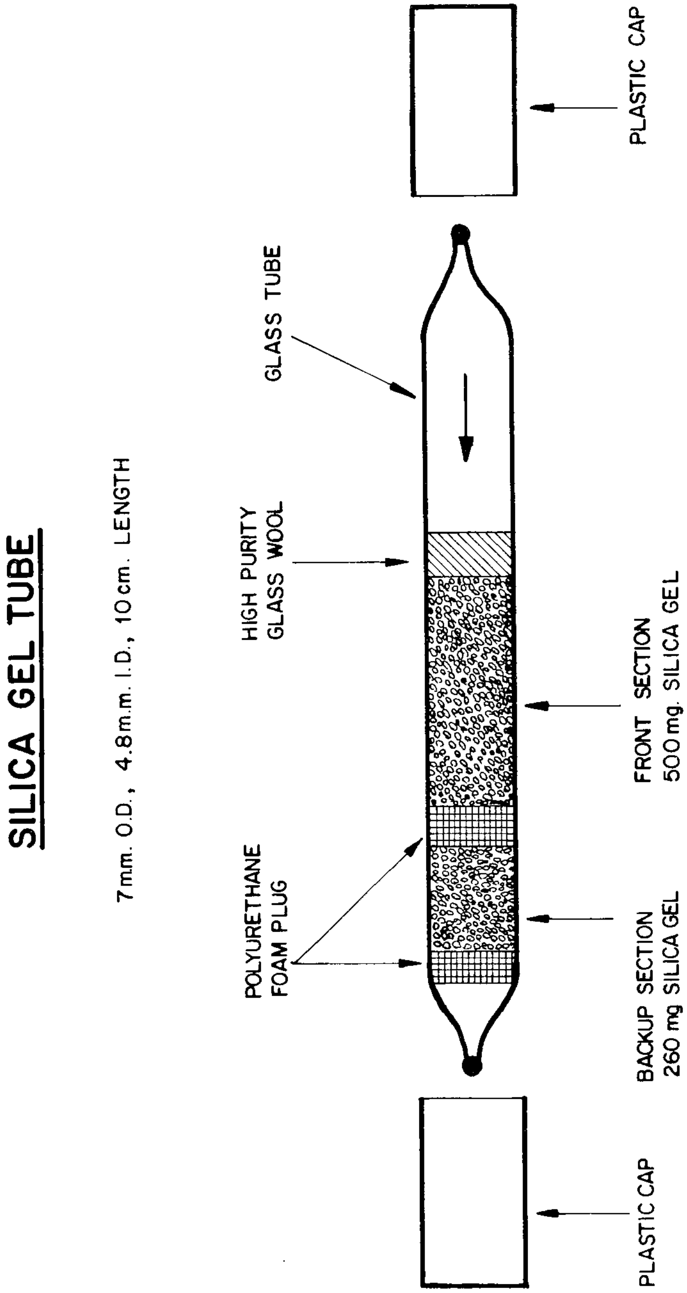
SILICA GEL TUBE
7mm. O.D., 4.8m.m. I.D., 10cm. LENGTH
PLASTIC CAP
BACKUP SECTION
260 mg SILICA GEL
POLYURETHANE
FOAM PLUG
FRONT SECTION
500mg. SILICA GEL
HIGH PURITY
GLASS WOOL
GLASS TUBE
PLASTIC CAP

FIGURE 1

260 mg in the backup section (the rest). This sampling procedure allows to collect vapors and particles together.

The air volume recommended for acid collection is fifty liters. The flow rate is 0.2 l/m for silica gel tubes and 2 l/m for filters.

The extraction procedure of filters is quick and easy. The filters are extracted with 10 ml of chromatographic eluent with occasional vigorous shaking for 30 min. After this time, an aliquot of sample can be directly injected into the chromatograph.

Results obtained in a study about the desorption efficiency cellulose and PVC filters are almost the same in both cases, between 96 and 99%.[14]

When the samples are collected with silica gel tubes, their desorption is different and more difficult.[13] The silica gel and glass wool plug from the front section of the collection tube are placed into a 15 ml, graduated centrifuge tube. (The backup section is analyzed separately). Add 5 or 6 ml of chromatographic eluent and heat in a 100°C water bath for 10 min.

Allow to cool and dilute to 10 ml volume with eluent. Cover with parafilm and shake vigorously. Filter and allow to settle during 30 min before injection of an aliquot of sample into the chromatograph.

The silica gel utilized in the collection of hydrochloric acid must be washed many times before sampling to prevent contamination.[13]

Determination of desorption efficiency

The desorption efficiency of a particular compound may vary between laboratories and batches of silica gel tubes or filters. For this reason its determination is necessary.

A known amount of the appropriate stock solution is injected into a silica gel tube or onto the filter and allowed to stand overnight to ensure complete adsorption of the acid under study. Subsequently, tubes, blanks and standards are desorbed as described above and are analyzed by Single Column Ion Chromatography.

The results obtained are shown in Table I. We could not study the desorption efficiency of Cl^- because silica was contaminated.

The desorption efficiency of $SO_4^=$ is studied at three levels representing 2, 1 and 0.5 of Threshold Limit Value (TLV). When the amount of $SO_4^=$ on the filter is small, ($\leq 25\,\mu g$/filter), efficiency decreases.

TABLE I

Desorption effeciences

Ion	Desorption Efficiency
Br^-	98%
NO_3^-	99%
$SO_4^=$	99% (86%)
Cl^-	Unknown

HPLC operating conditions

Typical operating conditions for inorganic acids analysis are: Mobile phase: 4×10^{-3} M aqueous silution of KHP, pH = 4.5. Stationary phase: Wescan Anion Column. Flow rate: 1 ml/min. Detector: Wescan conductivity detector. Injection volume: 100 μl.

With these conditions, retention times of different anions are: Cl^-: 3.2 min, Br^-: 5 min, NO_3^-: 6 min and $SO_4^=$: 12 min. Figure 2 shows a typical chromatogram of these anions obtained under the conditions described before.

RESULTS

Detection limits are presented in Table II. All of these are low enough for the application of this technique in industrial hygiene. Moreover chromatographic detection limits are like those found in the literature.[15] The variation coefficients at TLV-TWA concentration are also adequate. In this sense we must indicate the small value found for NO_3^- (0.9%).

Calibration plots are presented in Figure 3. The correlation coefficients are between 0.96 ($SO_4^=$ and Br^-) and 0.99 (NO_3^- and Cl^-).

These methods have been tested in several work place examinations.

CONCLUSIONS

The advantage of Ion Chromatography and particularly Single Column Ion Chromatography over other methods is its capability of

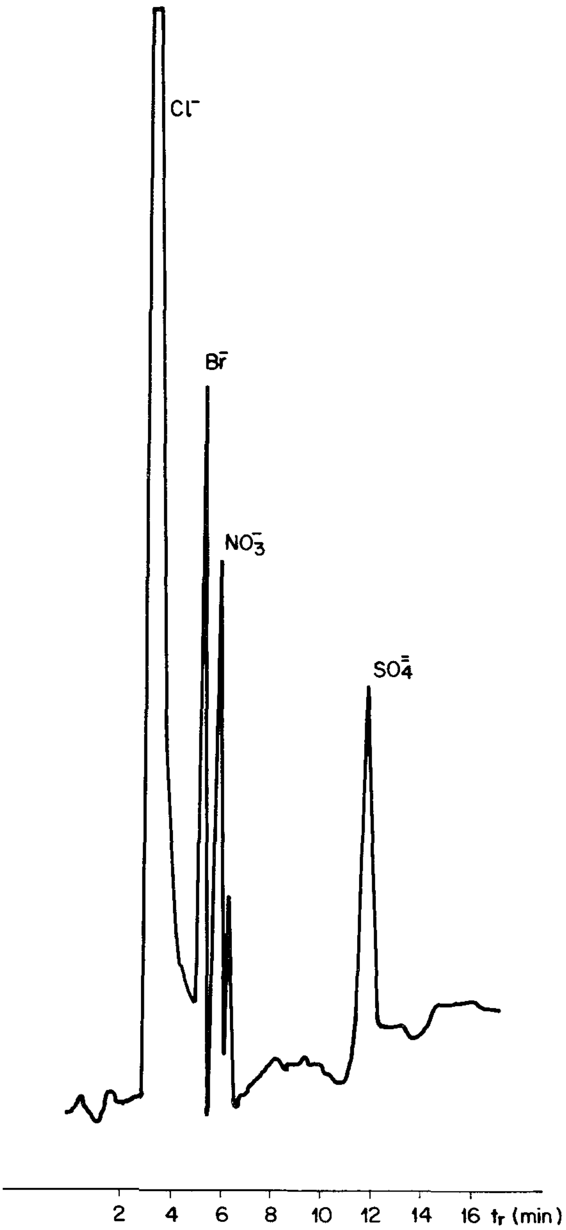

FIGURE 2 Chromatogram of the four anion standard.

TABLE II

Results

	Detection Limits				
Ion	Chromatographic	Tube o filter	Air	Variation coefficients (At TLV-TWA Levels)	TLV-TWA (ACGIH, 1984–5)
Cl^-	100 ng	30 μg	0.2 mg/m^3	4.8%	7 mg/m^3
Br^-	350 ng	35 μg	0.7 mg/m^3	4.4%	10 mg/m^3
NO_3^-	50 ng	5 μg	0.1 mg/m^3	0.9%	5 mg/m^3
$SO_4^=$	100 ng	10 μg	0.2 mg/m^3	6.9%	1 mg/m^3

Sampling volume = 50 litres

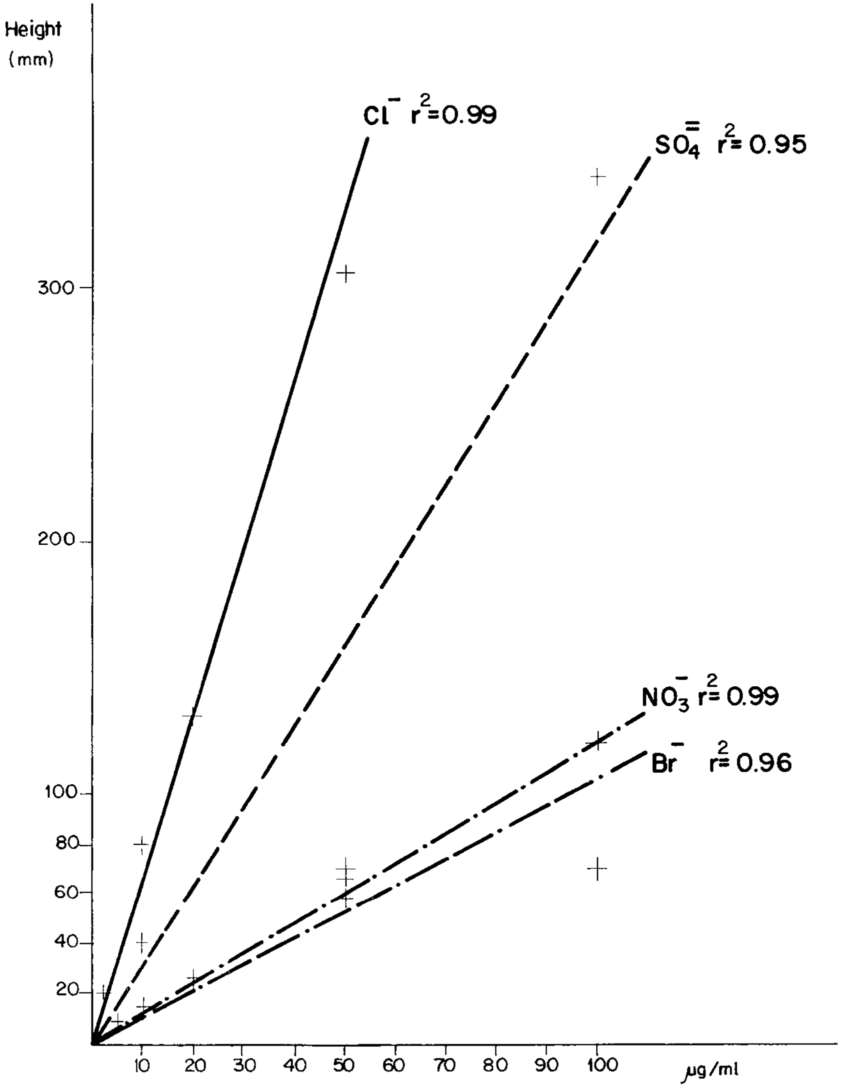

FIGURE 3 Calibration curves for chloride, sulfate, nitrate and bromide.

separating several ions so that each of the acid anions may be identified and measured in a single sample.

Moreover, the sampling device is a solid sorbent collection tube or filter and involves no liquids. Detection limits, desorption efficiences and variation coefficients are adequate for use in industrial hygiene. Ion chromatography without suppresor column allows a rapid and efficient analysis of samples.

Finally, the use of a conventional liquid chromatograph for the determination of inorganic acids in air is also a great economical advantage.

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