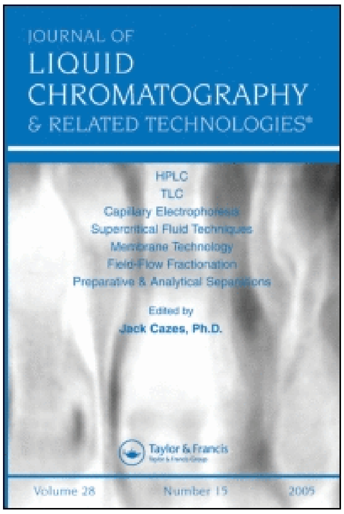

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DETERMINATION OF SILVER IODIDE BY HIGH PRESSURE ION CHROMATOGRAPHY IN SOIL AND WATER MATRICES AFTER SOLID PHASE EXTRACTION

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ABSTRACT

Silver iodide is determined in soil and water samples after reduction by zinc, in acidic with acetic acid environment at 60°C, for 2 h. Iodide ions are subsequently determined by High Pressure Ion Chromatography using a low capacity, PRP-X100 Hamilton 150 x 4.1mm, 10μm, anion exchange column filled with spherical poly(styrene-divinylbenzene)trimethylammonium exchanger, with a mobile phase consisted of CH_3OH-NaCl 0.1 M (55:45 v/v).

Identification of iodide ions was achieved by UV detection and quantitation was performed at 230 nm. Nitrate ions were used as internal standard at a concentration of 1.5 ng/μL. Limit of detection (S/N=3) was 0.8 ng for iodide ions. Recovery of iodide from silver salt was 95% with a reproducibility better than 6 % RSD. Recovery of silver iodide from spiked soil matrices was 90%.

Solid phase extraction, using SAX Lichrolut Merck cartridges, revealed recoveries of iodide ions ranging from 86 - 108%. Iodides were eluted from sorbent using a mixture of 70-30 % v/v 0.1M NaCl-CH_3OH as eluent.

Statistical evaluation of presented method was examined performing intra-day (n=8) and inter-day (n=8) calibration studies and was found to be satisfactory with high accuracy and precision results.

INTRODUCTION

Silver iodide is being used widely in weather modification programs throughout the world since the decade of 1970's, as a cloud seeding agent alternative to dry ice. It is usually dispensed as particles in the size range 0.01-1.0 μm diameter, chosen for the specific atmospheric properties, particularly in the nucleation of ice crystals or water droplets in clouds. It can be released into clouds from aircraft or dispersed from ground based generators, if atmospheric conditions are appropriate.

The pathways followed by silver iodide, after it reaches the ground, are uncertain. Accumulations of silver iodide from cloud seeding in soil, vegetation, and surface waters have to be measured by sensitive techniques, as the concentrations are usually low. It is also likely that the main amount of the silver iodide is trapped in the uppermost layers of the ground and that some of it is carried by percolating water or other transport processes to deeper layers of the soil or underwater muds where it is sequestered from the biosphere. The part of it that is trapped in the soil probably circulates in some degree through vegetation, litter, and back to the soil.[1]

In order to point out whether there is a potential of an aggregate impact of silver iodide from precipitation management activities on the quality of the environment, a precise and accurate method of silver iodide determination in soil samples has to be developed.

Halides can be liberated from silver halides by reduction, complexation, or ligand exchange with anions such as sulfide.

Gustafson et al.[2] have determined silver halides by Ion Exchange and Ion Interactive Chromatography, after reduction of silver in basic aqueous hydrazine solution according to the following reaction:

$$4AgX + 4OH^- + N_2H_{4(aq)} \longrightarrow 4Ag_{(s)} + 4X^- + 4H_2O + N_{2(g)}$$

Recovery of AgI reported was 92%. Sample preparation time was enhanced due to the 24 h reduction step in a heating block at 60-70°C necessary for iodide liberation. Hydrazine was further removed from the samples before introduction into column; due to its toxicity, concentrated hydrazine was handled in a hood. A hydrogen form, strong acid cation excange resin, converts sodium hydroxide and hydrazine into water. Iodide ions were analyzed by ion interaction chromatography with a 10 min analysis time.

Single column anion chromatography has been reported by Gjerde et al.,[3,4] as a method for the analysis of anions. Separation is performed on a low capacity column and is achieved by using a very dilute solution of an aromatic acid salt where electric conductivity detector is used to monitor anion peaks. This technique avoids the use of a suppressor column to eliminate background conductivity as was at first introduced by Small et al.[5]

Several papers have been published for iodide determination using various eluent systems. Iodide can be analyzed on a reversed phase C_{18} chromatographic column by using a dilute aqueous solution of tetrabutylammonium salicylate as eluent with conductivity detection.[6] Mangia et al. have analyzed iodide ions, among others, by means of ion-pair chromatography on a reversed phase column RP-2 Lichrosorb, using the tricaprylmethylammonium ion in an acetonitrile water mobile phase and UV detection at 226nm.[7] The sodium salt of methanesulphonic acid has been used for UV detection of iodide within 8 min.[8]

An HPLC method used micellar hexadecyltrimethylammonium chloride as mobile phase with C_{18} column and UV detection.[9]

The use of tetrabutylammonium hydroxide TBA-OH 10% acetonitrile, UV detection at 227nm was also reported.[10] Cetyl trimethylammonium bromide (cetrimide) has been used for ion-pair formation.[11]

Cetyl trimethylammonium-p-toluenesulphonate is used as mobile phase.[12] Iodide ions have also been analyzed on PRP-X100 macroporous poly(styrene-divinylbenzene) strong-base anion exchanger.[13-15]

A variety of different detection techniques, such as conductometry, amperometry, UV, refractive index, atomic absorption, and potentiometry are used in ion chromatography analysis.[16]

In the majority of publications, conductometric detectors were used and standard UV for direct or indirect detection of anions with two detectors in series.[12]

Indirect photometric UV detection, which relies on the decrease in the background UV absorption of the potassium hydrogen phthalate buffer as the individual anions are eluted, have been reported by Cochrane et al.[17] Thus detection limits were reduced to 0.5 ppm while, when using conductivity, it was 3 ppm when 100 μL were introduced into the column.

Post column fluorescence detection has been introduced by Lee et al. [18] for iodide anions determination, using their reaction with Ce(IV) to produce the fluorescent species Ce(III) in a postcolumn-packed bed reactor. Iodide anions are eluted in 15 min.

Electrochemical detection via a silver working electrode[19] has been reported by Rocklin et al. and by Mehra et al.,[16] with 200μL injection volume and a detection limit of 10ppb.

Iodide ions have been determined in soil extracts by Bowman via UV detection at 210 nm.[20] Soil samples were dried and passed through a 2mm sieve.[16] UV detection of iodide by RPC used mobile phase containing TBA-OH.[21]

Direct photometric detection of iodide, at 226 nm, was used, in contrast to the normally used conductivity or indirect UV detection. Detection limit in pure solutions was 10 ppb, with possible decrease by a preconcentration procedure.[22]

Ion interaction chromatography using PRP-Hamilton column in the presence of a tetraalkylammonium salt (R_4N^+) (dynamic ion exchange) was proposed by Iskandarani et al[23] for several inorganic ions, iodide, among them.

Low capacity anion exchange columns prepared by coating C_{18} reversed phase column with cetyl-trimethylammonium chloride were proposed by Ito et al.[24] with UV (at 226nm) or amperometric versus Ag/AgCl detection. The mobile phase consisted of 0.1M NaCl-5 mM sodium phosphate buffer (pH=5-8).

An alumina filled cartridge column combined with a silica based (R_4N^+) ion exchange column, is proposed by Buchberger et al.[25] for the determination of iodide in mineral water and juice samples. In this way, sample clean-up can be minimised and sensitivity of the chromatographic system allows determination of iodide down to the low ppb range.

A polymethacrylate based anion-exchange column and 0.1M NaCl-5mM sodium phosphate (pH=6,7) buffer as mobile phase by Ito et al.,[26] was used with UV and amperometric detection. Iodide has maximum UV absorbance at 226nm where the background absorbance of 0.1 M NaCl is low.

C_{18} bonded silica based RP column and mobile phase of 0.005M tetrabutylammonium hydrogen sulfate in methanol-phosphate buffer 15:85 was used. Detection was achieved by UV absorbance (direct oxidative ameprometric electrochemical or series configured dual electrode amperometric electrochemical detection). In addition, conductimetric detection with mobile phase of 0.9 mM tetrabutylammonium salicylate in methanol-water 10-90 have been employed.[27]

The most difficult part of many ion chromatographic applications is elimination of interfering components from the sample matrix. These compounds may overload the column, contaminate or mask peaks of interest, or may be retained irreversibly on the packing. Sample preparation is usually necessary to clean up samples prior to analysis. Solid phase extraction cartridges have been developed for IC.

Strong anion exchangers in OH^- form, are used to retain anions. Strong cation exchangers, in Ag^+ form, are used to retain chloride, iodide, bromide, through formation of Ag halide salts.[28]

Little work appears to have been done regarding HPIC analysis of AgI in soil samples.

This paper describes an HPIC method for the analysis of iodide ions using a low capacity strong anion exchange column PRP-X100 Hamilton, with UV detection at 230 nm. Iodide ions are liberated from silver iodide by reduction, using zinc dust and glacial acetic acid at 60°C for 2 h. Solid phase extraction using SAX cartridges has been applied for sample preconcentration or clean-up.

EXPERIMENTAL

Instrumentation

A Shimadzu (Kyoto, Japan) LC-9A pump was used to deliver the mobile phase to the analytical column; a strong anion exchange, low capacity, PRP-X100 Hamilton 150x4.1 mm 10μm with exchange capacity 0.19 ± 0.02 meq/g.

Sample injection was performed via a Rheodyne 7125 injection valve (Rheodyne, Cotati California,U.S.A) with a 20 mL loop. Detection was achieved by an SSI 500 UV-Vis detector (SSI, State College, PA, U.S.A.) at a wavelength of 230 nm, at a sensitivity setting of 0.002 AUFS.

A Hewlett-Packard (Avondale, PA, U.S.A.) HP3396 Series II integrator was used for quantitative evaluation of eluted peaks.

A glass vacuum-filtration apparatus obtained from Alltech Associates, was employed for the filtration of the buffer solution, using 0.2 μm membrane filters obtained from Schleicher and Schuell (Dassel, Germany).

Degassing of solvents was achieved by sonication in a Transonic 460/H Ultrasonic bath (Elma, Germany) prior to use.

A Glass-col, Terre Haute 47802 small vortexer and a Hermle centrifuge, model Z 230 (B. Hermle, Gosheim, Germany) were employed for the sample pre-treatment.

A Heraeus incubator (Hanau,Germany) was used for AgI reduction.

The SPE assay was performed on a Vac-Elut vacuum manifold column processor purchased from Analytichem International, a division of Varian (Harbor City, USA).

All evaporations were performed with a 9-port Reacti-Vap evaporator (Pierce, Rocford, IL, USA).

UV spectrum of iodide ions for selecting the working wavelength of detection was taken using a Varian DMS 100S UV/VIS double-beam spectrophotometer.

All computations were achieved using a VIP 312 computer.

Materials and Reagents

Potassium iodide, sodium chloride, sodium nitrate, and sodium bromide were purchased from Merck (Darmastadt, Germany) and were pro analysi grade.

HPLC grade methanol and acetonitrile were obtained from Lab-Scan (Dublin, Ireland). Silver iodide was prepared in the Laboratory of Analytical Chemistry, from silver nitrate p.a. and potassium iodide p.a., purchased from Merck. Glacial acetic acid p.a was also from Merck, as well as zinc dust <60μm. Bis de-ionised water was used throughout analysis. Solid phase extraction cartridges, SAX Lichrolut, were from Merck.

Standard Solutions

An aqueous stock solution of iodide ions, from potassium iodide, at a concentration of 100 mg/L was prepared and stored, refrigerated, at 4°C. This solution was found to be stable throughout experimental analyses.

Working aqueous solutions were prepared from stock solution at concentrations 0.25, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0, 10.0, 15.0, and 20.0 ng/μL.

Nitrate ions at a concentration of 1.5 mg/L were added as internal standard.

Chromatography

Peak areas of the iodide ions were measured and the ratio to internal standard was compared to that of the calibration standard.

The analytical column was maintained at ambient temperature.

RESULTS AND DISCUSSION

Optimisation of the Chromatographic System

The chromatographic system for determining iodide ions was chosen among others regarding the gradient time and eluent consistence.

A variety of binary mixtures of organic modifiers with NaCl in several ratios (Table 1) was tested to result in optimum chromatographic system.

The final mobile phase was chosen in terms of peak shape, column efficiency, chromatographic analysis time, selectivity, and resolution. Inlet pressure observed with the selected eluent system was 90-95 kg/cm^2.

Table 1

Optimum Conditions for the Chromatographic Analysis of Iodide Ions

NaCl (%)	Organic Modifier (%)	Retention Time (min)	Flow Rate (mL/min)
50	50 CH_3CN	11.5	2
55	45 CH_3CN	11.9	2
45	55 CH_3CN	12.8	2
60	40 CH_3CN	13.2	2
50	50 CH_3OH	10.2	1.5
50	50 CH_3OH	8.4	2
45	55 CH_3OH	9.5	1.5
45	55 CH_3OH	6.4	2
55	45 CH_3OH	9.4	1.5

The use of acetonitrile led to an increase of analysis time which enhanced the analysis cost. The optimum mobile phase as reported in Table 1 is consisted of CH_3OH-NACl 0.1M (55:45v/v). Figure 1 shows the chromatogram obtained using the conditions described in Table 1. Both bromide and nitrate ions can be characterised as suitable internal standards, as both absorb in UV region and have similar retention times with the eluent system used (3.36 min).

Nitrate ions were finally preferred, as bromide ions may also be liberated from reduction of silver bromide salt from soil samples.

The resolution factor between iodide and nitrate ions is 3.6.

Performance Characteristics of the Proposed Method

Optimised chromatographic conditions were set and the statistical evaluation of the proposed method was performed according to the following parameters:

- Analysis time.
- Calibration data.

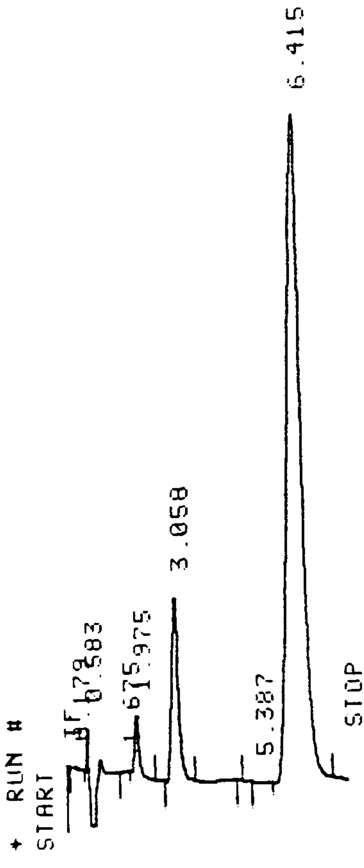

Figure 1. High Performance Liquid Chromatogram of iodide analysis with conditions described in text (3.058 min NO_3^-, 1.5 ppm, 6.415 min I^-, 2.0 ppm).

- Selection of wavelength.
- Working range and detectability.
- Precision and accuracy.
- Solid-phase extraction.
- AgI reduction.
- AgI recovery from soil samples.

Table 2

Calibration Data for Iodide Determination With and Without Nitrate as Internal Standard

Parameter	Value	With Internal Standard	Without Internal Standard
Concentration range	mg/L	0.25-20.0	
Slope	AIU/ng	2.59145±0.04400	1491575±3607.7
Concentration range	ng		0.5-10.0
Slope	AU/ng	0.12957±0.0220	74568.8±180.4
Intercept		-0.30131±0.21350	-121972±18708.7
Correlation coefficient		0.99914	0.99998
Detection limit	ng	0.8	0.8

Working Range and Detectability

The upper limit was found to be 20 mg/l, while detection limit calculated as a three fold signal to noise ratio at the baseline (S/N= 3) was found to be 0.8 ng for 20 μL injection volume.

Calibration Data and Analysis Time

The sample analysis time of iodide ions in the proposed method is 6.4 min.

Calibration of the method was performed by injection of standards covering the entire working range. Eight concentrations were used in the range 0.25 - 10 ng/μL.

The sensitivity setting of the UV detector was adjusted at 0.002 AUFS. Each sample was injected five times.

Linear correlation between absolute injected amount or concentration and peak area ratio with nitrate as internal standard at a concentration of 1.5 ng/μL was observed, as well as, for absolute peak area of iodide when nitrate were not added or not taken into account as internal standard. The results of the statistical treatment of calibration data are summarised in Table 2.

Table 3

Within-Day Precision and Accuracy for Iodide Determination (n=8)

Amount of Iodide Anions Added (ng)	Amount of Iodide Anions Found (ng)	SD (ng)	RSD (%)
20	19.70	0.64	3.25
40	39.87	1.18	2.96
60	60.36	2.17	3.60
100	99.80	4.72	4.73

Selection of Wavelength

The analytical wavelength 230 nm was chosen for quantitation though iodide ions show a maximum absorbance at 226 nm. The selection of a slightly higher wavelength was preferred in terms of faster column equilibration time.

Precision and Accuracy

Method validation regarding reproducibility was achieved by replicate injections of standard solutions at low and high concentration levels where peak areas were measured in comparision to the peak area of the internal standard.

Statistical evaluation revealed relative standard deviations at different values for eight injections. Results are shown in Table 3. Long term stability study was conducted during routine operation of the system over a period of eight consecutive days. Results are illustrated in Table 4.

Solid Phase Extraction of Iodide Ions

Strong anion exchange Lichrolut (Merck) cartridges were used for iodide preconcentration or sample clean up procedure. Cartridges were conditioned with 3 mL of CH_3OH and 3 ml of NaCl 0.05 M.

Table 4

Day-to-Day Precison and Accuracy for Iodide Determination Over a Period of 8 Consecutive Days

Amount of Iodide Anions Added (ng)	Amount of Iodide Anions Found (ng)	SD (ng)	RSD (%)
20	19.99	0.52	2.60
40	40.37	0.50	1.24
60	61.15	1.62	2.65

An aliquot of 10 ml of standard solution was applied to the cartridge and iodide were eluted by flushing the cartridge with 1ml of a mixture consisted of 0.1 M NaCl - CH_3OH 70-30 % V/V. Then the sample was either injected onto the column or evaporated to dryness under gentle nitrogen steam in a 45°C water bath and diluted to 100μL with the internal standard solution.

Extraction efficiency was calculated by extracting standard solutions of iodide ions at five different amount levels ie 0.5, 1.0, 2.0, 5.0, and 10.0 ng.

Recovery of compounds was calculated by comparing peak area ratios against internal standard with those obtained for unextracted solutions. Results obtained are presented in Table 5.

Silver iodide reduction

For silver iodide reduction 1mL of glacial acetic acid, 5g of zinc dust and 40 mL of de-ionised water were added to approximately 0.05g of AgI.

After heating to 60°C for 2 h in an incubator, silver reduction is completed according to the equation:

$$2AgI_{(s)} + Zn_{(s)} \rightarrow 2Ag_{(s)} + ZnI_2$$

The sample is subsequently filtered and diluted to 100mL volume with water yielding an approximately 270 ppm I^- solution; with the proper dilutions, solutions within the working range are prepared and determined with the proposed method for iodide analysis.

Table 5

Recovery of Iodide Anions After SPE Using SAX Lichrolut Cartridges

Iodide Amount Added (ng)	Iodide Amount Found (ng)	SD (n=5) (ng)	RSD (%)	Recovery (%)
0.5	0.54	0.03	5.56	108.0
1	0.94	0.02	2.13	94.0
2	2.05	0.03	1.46	102.5
5	4.53	0.17	3.75	90.6
10	8.60	0.23	2.67	86.0
Recovery of Iodide Anions From AgI After Reduction				
17.1	17.1	0.3	1.75	100.0
34.2	29.5	0.5	1.69	86.3
64.8	58.0	1.4	2.41	89.5
18.8	20.5	0.7	3.75	109.0
37.6	35.8	1.1	3.07	95.2
75.2	71.6	2.1	2.93	95.2
21.9	20.8	1.2	5.77	95.0
43.8	38.0	2.1	5.53	86.8
87.8	93.8	3.7	3.94	107.1
108.0	106.3	1.6	1.50	98.4
53.4	48.4	2.8	5.78	90.6
106.8	98.6	4.6	4.66	92.3

Each sample was injected five times and results obtained are presented in Table 5. As shown in Table 5 iodide recovery from silver reduction is very satisfactory (mean value 95.45% ± 7.23). Chromatogram obtained from the reduction of AgI is illustrated in Figure 2.

Solid phase extraction of iodide after silver reduction

After silver iodide reduction two solutions in the working range are prepared from stock solution of iodide 270 ppm, namely 2.7 and 5.4 ppm. These solutions are subsequently treated by solid phase extraction according to the procedure described under the respective paragraph. Results are illustrated in Table 6.

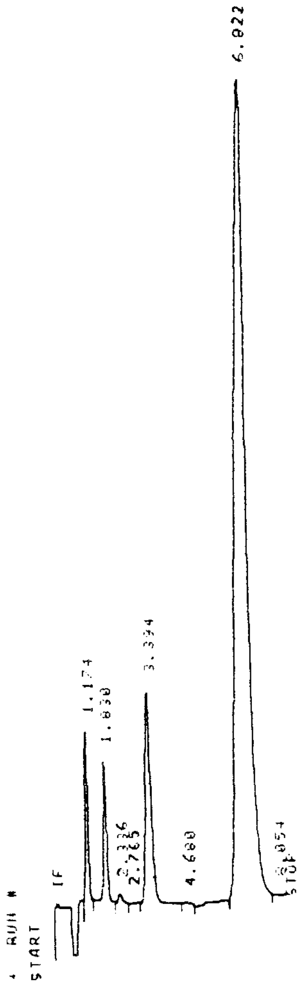

Figure 2. High Performance Liquid Chromatogram of iodide analysis after reduction of AgI. For details see in the text.

Silver iodide determination in soil samples

Five different soil samples of 5g ± 0.1 mg dry weight (fraction<2 μm) were treated with the reduction system described above.

Table 6

Recovery of Iodide Anions From Reduced AgI After SPE Using SAX Lichrolut Cartridges

Iodide Amount Added (ng)	Iodide Amount Found (ng)	SD (n=5) (ng)	RSD (%)	Recovery (%)
54.0	45.6	0.9	1.97	84.44
108.0	93.2	2.1	2.25	86.30
Recovery of Iodide Anions From Reduced AgI After SPE Using SAX Lichrolut Cartridges With Nitrate Anions as Internal Standard				
54.0	51.0	3.1	6.08	94.44
108.0	101.8	5.1	5.00	94.26

For each soil sample the following procedures were performed:

a) The soil was treated as described for silver reduction.

b) The soil was initially washed out with de-ionised water to remove water soluble iodide ions and subsequently treated as described above.

c) The soil sample was washed to remove water soluble iodide ions and 0.05 g of AgI were added. The sample was subsequently treated for silver reduction.

d) The soil sample was spiked with 0.05 g AgI and subsequently trated for silver reduction.

Results obtained are presented in Table 7.

Figure 3 shows the chromatogram of a soil sample spiked with AgI.

CONCLUSIONS

A high pressure ion chromatographic technique was developed for the determination of iodide ions with UV detection.

A strong anion exchange PRP-X100 Hamilton column was used for iodide retention and a mixture of 0.1M NaCl- CH_3OH 45:55 % v/v was used for elution at a flow rate 2 mL/min.

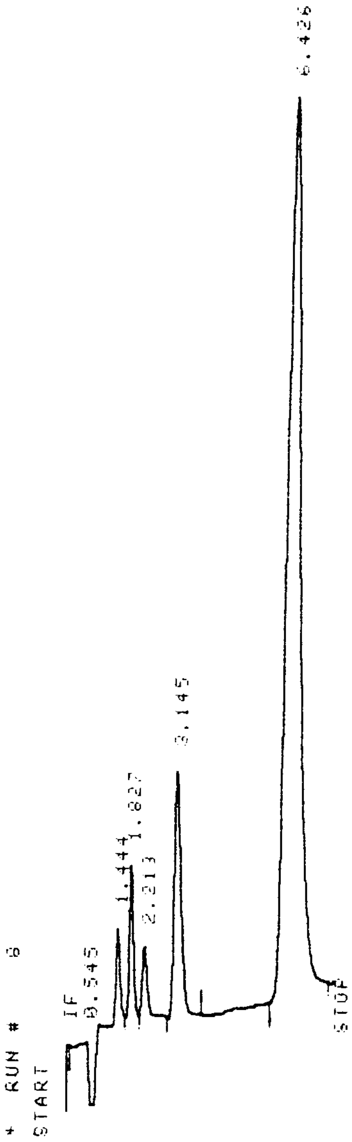

Figure 3. High Performance Liquid Chromatogram of iodide analysis in soil samples spiked with AgI. For details see in text.

Table 7

Recovery of AgI From Spiked Soil Samples

Iodide Concentration in Soil (μg/g)	AgI Concentration Added (ppm)	AgI Concentration Found (ppm)	SD (n=5) (ppm)	RSD (%)	Recovery of AgI From Soil (%)
4.1	2.82	2.21	0.09	4.07	78.4
8.6	3.01	2.84	0.11	3.87	94.4
4.2	2.76	2.33	0.11	4.72	84.4
4.1	2.70	2.98	0.06	2.01	110.4
6.5	2.80	2.31	0.08	3.46	82.5
Recovery of AgI From Spiked Prewashed Soil Samples					
2.0	2.98	2.89	0.08	2.77	96.9
2.0	2.70	2.87	0.10	3.48	106.3
2.2	3.00	2.48	0.14	5.64	82.7
3.8	3.20	3.07	0.09	2.93	95.9
7.1	3.01	2.15	0.10	4.65	71.4

Solid phase extraction technique with SAX Lichrolut cartridges was applied for sample preconcentration or clean-up procedure which provided selective recovery of iodide ions. For AgI reduction in order to liberate iodide ions, 5g of zinc dust, 1mL of glacial acetic acid and 40 mL of de-ionied water were added to sample.

After 2 h heating at 60°C an almost complete recovery of iodide was observed (~95%). This reduction system shows significant advantages towards the unique published method proposed by Gustafson et al.[2] that uses hydrazine which demands 24 h heating and special care due to the high toxicity of hydrazine.

Limit of detection of iodide is 0.8 ng for 20 μL injected sample volume. Day - to - day precision was tested over 8 consecutive days, and repeatability (within day run) proved to be very satisfactory (RSD < 6 %).

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