# Matrix Elimination Ion Chromatography Method for the Determination of Trace Levels of Anionic Impurities in High Purity Cesium Iodide

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In the present study an ion chromatographic method based on matrix elimination has been developed for the determination of anionic impurities in high purity cesium iodide crystals. The presence of impurities has a detrimental effect on the characteristics of detectors based on cesium iodide crystals. In particular, oxygen-containing anions inhibit the resolving power of scintillators and decrease the optical absorption. The quantitative determination of anions (fluoride, chloride, bromide, nitrate, phosphate, and sulphate) simultaneously in the high-purity cesium iodide crystals has not been carried out before. The large concentration of iodide poses a challenge in the determination of anions (especially phosphate and sulphate); hence, matrix elimination is accomplished by adopting a sample pretreatment technique. The method is validated for linearity, accuracy, and precision. The limit of detection for different anions is in the range of 0.3–3 $\mu$g/g, and the relative standard deviation is in the range of 4–6% for the overall method.

## Introduction

Cesium iodide finds wide applications in scintillation detectors, X-ray imaging systems, infrared prisms, and cell windows. The scintillation characteristics of cesium iodide crystals depend on both the crystal purity and perfection (1, 2). The presence of unwanted impurities in the crystal can modify the light emission of the scintillator, thus affecting its performance in terms of energy resolution. Anionic impurities give rise to conductivity of cesium halides in the extrinsic region whereas cationic impurities cause a conductivity decrease resulting from trapping of the main carriers (anion vacancies) by the cation vacancies (3). Hence, highly pure starting material is needed for cesium iodide crystal preparation. Several methods have been successfully used for the purification of the cesium iodide (4). However, little work has been done to quantify the anionic impurities in purified cesium iodide crystals.

Few researchers have reported the presence of anions in cesium iodide, but no effort was made to quantify their concentrations. Hartmanova et al. have reported that the IR spectra of cesium iodide samples always showed the absorption bands at 1100, 1380, and 3650 cm$^{-1}$ corresponding to the presence of $SO_4^{-2}$, $NO_3^-$, and $OH^-$ groups, respectively (5). While Garapyn et al. in their study on different purification methods have reported that the absorption bands for typical anionic impurities such as $NO^{-3}$, $CO_3^{-2}$, and $OH^-$ were absent in the IR spectra of the cesium iodide crystals (4). Recently, PIXE has been used to check the concentration of thallium dispersed in cesium iodide crystals. In this study, the authors reported the

presence of bromine in some of the examined crystals (6). Mikhailova et al. have reported the presence of phosphate-ion impurity in cesium iodide (7). Thus, there is not a single report in the literature on the determination of all the anionic impurities (i.e., $F^-$, $Cl^-$, $Br^-$, $NO_3^-$, $PO_4^{-3}$, and $SO_4^{-2}$) in high-purity cesium iodide crystals. Hence, the aim of this study was to develop a simple, rapid, and accurate method for the simultaneous determination of different anions in cesium iodide crystals.

Ion chromatography with conductometric detection is an instrumental technique for the simultaneous determination of anions, particularly at trace concentrations (8, 9). In case of cesium iodide the presence of a large concentration of iodide matrix poses a challenge in the determination of phosphate and sulphate anions. Hence, in the present work a single step sample pretreatment procedure was adopted to eliminate the matrix interference. The method was applied to different batches of high purity cesium iodide crystal preparation.

## Experimental

### Reagents

Cesium iodide was obtained from Merck and stored in a dessicator. All other reagents were of analytical grade and obtained from Sarabhai M. Chemicals (Baroda, India). The working standard and spiking solutions were prepared by dissolving sodium salt in 18 M $\hat{\Omega}$ deionized water (Barnstead, Boston, MA). OnGuard-Ag cartridges were obtained from Dionex (Sunnyvale, CA). They have a capacity of 2.0–2.5 meq/cartridge on a water swollen basis.

### Instrumentation

The ion chromatographic instrument from Metrohm (Herisau, Switzerland) consisting of a 709 IC Pump, 733 IC Separation Center, an MSM Suppressor with 752 Pump unit, and a 732 IC conductivity detector was used for the analysis. Anion separation was carried out in suppressor mode on a Metrosep A Supp 3 analytical column (25 mm x 4.6 mm) connected in series with a Metrosep RP guard column (75 mm x 4.6 mm). A solution containing a mixture of 1.8 mM $Na_2CO_3$ and 1.7 mM $NaHCO_3$ flowing at a rate of 1.0 mL/min served as the mobile phase. The relative ratios of the two solutions $Na_2CO_3$–$NaHCO_3$ in the mobile phase is 1.06. These are the standard operating conditions for the column: Metrosep A Supp 3 (with chemical suppression). A solution of 20 mM $H_2SO_4$ was used as the regenerant. The volume of the sample injection loop was 20 $\mu$L.

## Procedure

OnGuard-Ag cartridge was first washed with 10 mL deionized water. Approximately 5 mL of the sample solution was loaded on the cartridge and allowed to flow at a rate of 2 mL/min. The first 3 mL was rejected, and the next 2 mL was collected for direct injection into the ion chromatograph. This was done to ensure that there was no dilution of the sample solution during the pretreatment procedure.

## Results and Discussion

### Preparation of cesium iodide solution

The mass of cesium iodide to be used for the preparation of the solution was determined by the concentration of anions in the sample solutions so that a measurable signal could be obtained for the different anions. It was found that the peak signals for the different anions were measurable at 1% concentration of cesium iodide solution. Hence, 1% cesium iodide solution was used for the studies.

### Matrix elimination using OnGuard-Ag cartridge

The oxygen-containing impurities lead to the formation of complexes with activator ions (e.g., Tl) (10). Hence, there is a need to measure the trace concentrations of nitrate, phosphate, and sulphate in the cesium iodide crystal. Figure 1 shows the typical chromatogram of a standard mixture of anions: fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulphate at 2 μg/mL concentrations. The chromatogram of the 1% cesium iodide solution is shown in Figure 2. It is clear from the Figure 2 that the high quantity of iodide masks the phosphate ($t_r = 7.45$ min) and sulphate ($t_r = 8.09$ min) anion peaks and takes a long time for elution (5 min) from the column. In order to overcome these difficulties, matrix elimination using a simple and rapid pretreatment procedure was developed. For this, a commercially available OnGuard-Ag cartridge was used. The cartridge contains a high capacity, strong acid cation exchange resin in silver form. It removes iodide, chloride, and bromide anions by precipitation. When an aliquot of cesium
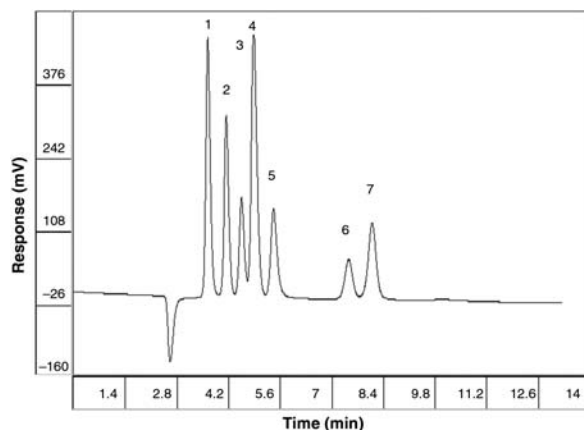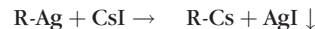
iodide solution was passed through the OnGuard-Ag cartridge, the cesium ions exchange with Ag ions and remain in the column while the iodide was precipitated within the cartridge as AgI by the following reaction:

$$\text{R-Ag} + \text{CsI} \rightarrow \quad \text{R-Cs} + \text{AgI} \downarrow$$

Thus, the cartridge was useful to remove the matrix ions quantitatively, provided that the concentrations of the ions were below the total capacity of the packing material of the cartridge. Each cartridge can be used for treating 9 mL of 1% cesium iodide solution. The solution emerging out of the cartridge was used for the determination of anions by injecting into the ion chromatography system. The different anions identified in the treated cesium iodide samples were fluoride, chloride, phosphate, and sulphate based on comparisons with that of standard anion mixture (Figure 3). The dip appearing after the chloride peak is due to the eluent anions (carbonate) and called the system peak (11). It is seen that phosphate and sulphate peaks are well separated from each other and the system peak. In the absence of a standard reference material,
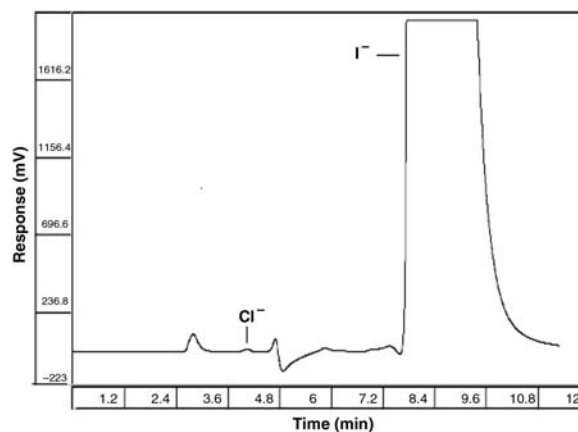
**Figure 2.** Chromatogram of the 1% cesium iodide solution showing masking of phosphate and sulphate anion peaks by large iodide peak. Eluting conditions: 1.8 mM $Na_2CO_3$ and 1.7 mM $NaHCO_3$ as eluent, flow rate of 1.0 mL/min.
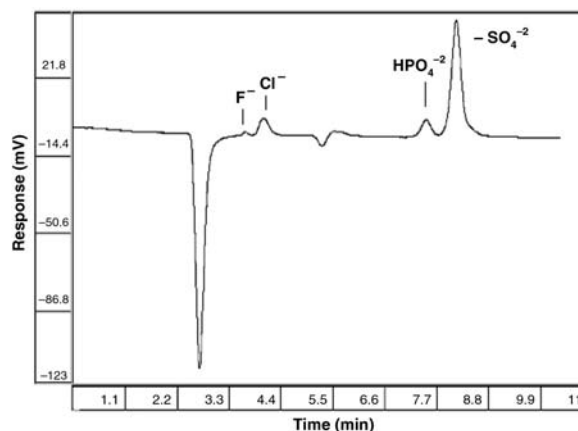
**Figure 3.** Chromatogram of the OnGuard-Ag treated cesium iodide solution showing fluoride, chloride, phosphate, and sulphate peaks using 1.8 mM $Na_2CO_3$ + 1.7 mM $NaHCO_3$ as eluent and a flow rate of 1.0 mL/min.

**Figure 1.** Typical separation of anion standard solution (2 μg/mL) showing: 1, fluoride; 2, chloride; 3, nitrite; 4, bromide; 5, nitrate; 6, phosphate; and 7, sulphate peaks. Eluting conditions: 1.8 mM $Na_2CO_3$ and 1.7 mM $NaHCO_3$ as eluent, with a flow rate of 1.0 mL/min.

**Table I**
Recovery of Anions in CsI Sample

| Anion | Added (μg/mL) | Found (μg/mL) | % Recovery |
|---|---|---|---|
| $F^-$ | 0.5 | 0.52 | 104 |
| $F^-$ | 1 | 0.98 | 98 |
| $PO_4^{-3}$ | 1 | 0.96 | 96 |
| $PO_4^{-3}$ | 5 | 5.2 | 104 |
| $SO_4^{-2}$ | 5 | 5.1 | 102 |
| $SO_4^{-2}$ | 10 | 9.8 | 98 |

**Table II**
Different Parameters Obtained Using Standard Anion Mixture Solutions

| Anion | Linearity range (μg/mL) | $r^2$ | LOQ (μg/mL) | LOD (μg/mL) |
|---|---|---|---|---|
| $F^-$ | 0.03–100 | 0.997 | 0.02 | 0.005 |
| $Cl^-$ | 0.03–100 | 0.998 | 0.02 | 0.005 |
| $Br^-$ | 0.03–100 | 0.997 | 0.03 | 0.01 |
| $NO_3^-$ | 0.03–100 | 0.998 | 0.03 | 0.01 |
| $HPO_4^{-2}$ | 0.03–100 | 0.999 | 0.03 | 0.01 |
| $SO_4^{-2}$ | 0.03–100 | 0.998 | 0.03 | 0.01 |

**Table III**
Anionic Impurities in CsI Sample

| Sample | Concentration of anions (μg/g) | | | |
|---|---|---|---|---|
| | Fluoride | Chloride | Phosphate | Sulphate |
| CsI.A | N.D.* | 70.0 ± 2.8 | 15.0 ± 0.9 | 189.0 ± 9.5 |
| CsI.B | N.D.* | 60.0 ± 2.4 | 13.0 ± 0.8 | 174.0 ± 8.7 |
| CsI.C | 0.5 ± 0.03 | 8.0 ± 0.3 | 21.3 ± 1.3 | 170.0 ± 8.5 |
| CsI.D | 0.5 ± 0.03 | 3.0 ± 0.1 | 15.0 ± 0.9 | 160.0 ± 8.0 |

* ND: not detected

identification and quantification of these anions were performed by determination of recovery from spiked solutions. The cesium iodide solutions were spiked with different concentration of anions (0.5–10 μg/mL) before pretreatment. The recovery values for different anions added (fluoride, phosphate and sulphate ions) were in the range of 96–104% (Table I).

The fluoride and sulphate ions were not retained on the OnGuard-Ag cartridge due to the higher solubility of their silver salts. The non-retention of phosphate ions was attributed to a high concentration of iodide ($10^6$: 1 iodide to phosphate). There was no peak obtained for the nitrate anion ($t_r$ = 5.42 min). This indicates that the nitrate, if present, was in the concentrations below the detection limits.

### Method validation
The limit of detection (LOD) (S/N = 3), limit of quantitation (LOQ) (S/N = 10), and linear range of calibration for different anions are given in Table II. The calibration graphs of peak areas for all anions are linear over two or three orders of magnitude with a regression coefficient ($r^2$) of 0.997–0.999. The relative standard deviations of different anions evaluated by replicate analysis ($n = 4$) in the cesium iodide samples were <6% (Table III). The best obtainable reproducibility limits of ion chromatographic methods of water analysis are in the range of 5–10% (12).

### Determination of chloride in cesium iodide crystals
The chloride anion in the cesium iodide crystals was determined by injecting 1% cesium iodide solution into the ion chromatography system directly (Figure 2). There was no peak observed for bromide ($t_r$ = 4.88 min.).

Table III presents the results of the different anion concentrations obtained in commercial and purified cesium iodide crystals (CsI.A, B, C, and D are the different samples provided by the Chemistry Division, BARC, Mumbai, India).

### Conclusion
The study showed that an OnGuard-Ag cartridge could be used successfully for the matrix elimination and ion chromatographic determination of fluoride, chloride, bromide, nitrate, phosphate, and sulphate ions in the cesium iodide crystals. The proposed method has several advantages. It is possible to identify and quantify the different anions simultaneously and with lower detection limits.

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