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**L'ÉNERGIE ATOMIQUE  
DU CANADA LIMITÉE**

**ANALYSIS FOR IODIDE IN GROUNDWATER BY  
X-RAY FLOURESCENCE SPECTROMETRY AFTER  
COLLECTION AS SILVER IODIDE ON  
ACTIVATED CHARCOAL**

**ANALYSE POUR DETERMINER L'IODURE DANS L'EAU  
SOUTERRAINE PAR SPECTROMETRIE DE LA  
FLOURESCENCE X APRES RECUEIL SUR CHARBON  
ACTIF SOUS FORME D'IODURE D'ARGENT**

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**Etablissement de Recherches  
Nucléaires de Whiteshell**

**Pinawa, Manitoba R0E 1L0  
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RESUME

Le rapport décrit la détermination de quantités d'iodure de l'ordre du microgramme dans l'eau par spectrométrie de la fluorescence X. L'iodure est concentré par précipitation sur charbon actif sous forme d'iodure d'argent. Si on dispose d'un échantillon de 60-mL, on peut détecter une concentration de 0.12 mg/L. La précision (2 $\sigma$ ) au niveau de 1 mg/L est de  $\pm$  0.08 mg/L.

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ABSTRACT

The report describes the determination of microgram quantities of iodide in water by X-ray fluorescence spectrometry. The iodide is concentrated by precipitation as silver iodide on activated charcoal. If a 60-mL sample is available, a concentration of 0.12 mg/L can be detected. Precision ( $2\sigma$ ) at the 1-mg/L level is  $\pm 0.06$  mg/L.

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## 1. INTRODUCTION

The concentration of iodide in water is of general interest. For example, the ratio of iodide to bromide in groundwater is indicative of the origin of that groundwater<sup>(1)</sup>. It is of particular interest in connection with the disposal of radioactive products in deep underground vaults. A knowledge of the iodide concentration in underground waters which may be in contact with immobilized waste is important, since it may affect the rate at which some radionuclides are leached from the stored material or transported through the surrounding rock.

While the concentration of iodide in water can be measured gravimetrically<sup>(2)</sup>, by its redox reactions<sup>(2,3)</sup>, by amperometric or coulometric titrations<sup>(2)</sup>, or by ion chromatography, the most widely applied methods are the ceric sulfate/arsenious acid colorimetric<sup>(4,5)</sup> and the potentiometric ones, the latter based on an iodide ion selective electrode<sup>(3,6)</sup>. Neither of these more commonly used methods is completely satisfactory for the determination of iodide in groundwater. Fluoride and irca, at the concentrations typically found in groundwater, interfere with the colorimetric method and a potentiometric titration using an iodide ion selective electrode to sense the end point is not adequately sensitive<sup>(3,7)</sup>. A direct determination using the same electrode is satisfactory in distilled water, but was found to show a pronounced positive bias in a synthetic groundwater medium.

This paper describes a sensitive method which has been developed and is now used at the Whiteshell Nuclear Research Establishment for the determination of the iodide concentration in either fresh or saline groundwater.

## 2. EXPERIMENTAL PROCEDURE

The  $I^-$  in the sample is precipitated as AgI on finely divided activated charcoal, which is collected on filter discs. After air drying, these discs are mounted in a spectrometer and their X-ray fluorescence is measured.

### 2.1 SEPARATION OF IODIDE FROM THE SAMPLE

Samples of groundwater are passed through Type HA 0.45  $\mu$ m Millipore filter discs to remove particulate material. This is normally done in the field shortly after the sample is taken. A known volume of sample ( $\sim 60$  mL is convenient) is transferred to a beaker containing a small Teflon-coated stirring bar. The beaker is placed on a magnetic stirrer where the sample is acidified to pH  $\sim 1$  (wide-range test paper) with  $HNO_3$ . The addition of 0.25 mL of the concentrated acid has been adequate for any samples so far received. After acidification,  $\sim 150$   $\mu$ g of activated charcoal are added. This is most conveniently done by adding a 50  $\mu$ L aliquot of a suspension of activated charcoal in demineralized water to the sample, using a suitably sized pipet. The suspension will mix readily if the tip of the pipet is beneath the surface of the sample when the suspension is discharged. Finally, 1.0 mL of an acidified (pH  $\sim 1$ ) solution containing 200  $\mu$ g Ag as  $AgNO_3$  is added.

One minute after the  $AgNO_3$  addition, the sample is passed through a second Type HA 0.45  $\mu$ m Millipore filter. The material collected is not washed, as this would disturb its uniform distribution on the filter disc. The disc is immediately mounted in a sample holder from the spectrometer to keep the disc flat as it is being air dried. As the material collected is adherent, the disc is not covered with Mylar film but is mounted so that the material collected is directly exposed to the primary beam of X-rays.

## 2.2 PREPARATION OF THE ACTIVATED CHARCOAL SUSPENSION

The suspension of activated charcoal is prepared by grinding commercially available 6-14 mesh material (Activated Coconut Charcoal, Fisher Scientific Co. Ltd.) with a mortar and pestle, or more conveniently in a mechanical shaker. A small amount ( $\sim 3$ g) of this ground material is moistened with methanol and transferred to a 200-mL graduated cylinder. The cylinder is nearly filled with demineralized water, the activated charcoal and water are mixed, and the suspension is left to settle. After approximately 30 minutes, 50 mL of the suspension are siphoned from the center of the graduated cylinder. This is the suspension that is added to the samples.

## 2.3. CALIBRATION

Calibration is by means of known quantities of  $I^-$  added to either approximately 60 mL of demineralized water, dilute (1%) NaCl or KCl solutions, or to a synthetic groundwater, all of which were treated as indicated above. The composition of this AECL Reference Synthetic Groundwater is given in Table 1.

## 2.4 X-RAY FLUORESCENCE MEASUREMENT

The fluorescence of the precipitate on each filter disc is measured with a Philips Universal Vacuum Spectrograph using these standard conditions:

1. A tungsten target operated at 50 kV and 40 mA.
2. The rotating sample mode.
3. A LiF (200) analyzing crystal.



4. A scintillation detector operated at  $\sim 750$  V.
5. The analytical line at  $2\theta = 12.34^\circ$  (I K $\alpha$ 1).
6. Background at  $2\theta = 11.80^\circ, 13.00^\circ$ .
7. The sample chamber and radiation path are not evacuated.

Three 10-second counts are averaged for each determination. The background count rate taken is the average of the count rates at the angles indicated.

### 3. RESULTS AND DISCUSSIONS

The response to  $I^-$  ions in the media of interest is shown in Figure 1. The precision ( $2\sigma$ ) of the method is  $\pm 5 \mu\text{g}$  at the  $50 \mu\text{g}$  level. This is equivalent to  $\pm 80 \mu\text{g } I^-/\text{L}$  in the 60-mL samples used.

As the response to higher concentrations of  $I^-$  is not linear (see Figure 2), those samples containing greater than  $700 \mu\text{g}$  of  $I^-$  ions in a 60-mL volume should be diluted. This non-linear response at higher concentrations is probably the result of the absorption of some of the fluorescent X-rays by the rather thick layer of AgI collected.

Interferences to this analysis are not expected from unresolved fluorescence peaks. With the exception of tellurium, elements which fluoresce at similar energies to  $I_2$  do not form insoluble silver compounds and so will not be collected on the filter disc. If tellurium is present, its K $\alpha$ 1 ( $2\theta = 12.80^\circ$ ) and K $\alpha$ 2 ( $2\theta = 13.00^\circ$ ) fluorescence peaks could interfere at the higher background angle used. These peaks would be detected on scanning the sample, and their effect can be avoided by using only the counting rate at  $2\theta = 11.80^\circ$  as the background. However, interference from  $S_2O_3^{=}$ ,  $CN^-$  and  $NH_4^+$  is expected as the AgI precipitate is soluble in a solution containing any of these ions.

The effect of  $S_2O_3^{2-}$  is shown in Figure 3. Only 10 mg/L can be tolerated before the response is lowered by an amount equivalent to the precision (2σ) of the method. It is unlikely that  $S_2O_3^{2-}$  would be found in groundwater but, if present, even at the 10 mg/L level, the elemental S formed when the sample is acidified will be seen on the filter disc; the precipitate collected will appear markedly whiter than that collected from the standard solutions.

While it is also unlikely that  $CN^-$  would be found in groundwater, it may be present in other samples. At least 120 mg/L can be tolerated, probably because it is eliminated as HCN when the sample is acidified. At least 700 mg  $NH_4^+$ /L (added as  $NH_4OH$ ) can be tolerated. This is also likely to be a result of sample acidification. Salt concentrations up to 5% (as KCl) do not interfere, but the  $I^-$  recovery from a 10% KCl solution is poor (approximately 20%). Each of the solutions used for these interference evaluations contained 50 μg  $I^-$  as KI.

The initial counting rate is higher for a given  $I^-$  concentration when activated charcoal is present. The activated charcoal may improve the efficiency of the AgI collection by providing nucleation sites or by adsorption of the precipitate. Its second and more important function is to retain the elemental  $I_2$  produced from the AgI by the exciting X-rays. If the activated charcoal is not added, the counting rate for a given amount of  $I^-$  drops by approximately 60% during the five minute exposure required to measure the fluorescence of the sample. The counting rate is maintained for at least 20 minutes when activated charcoal is used.

Approximately two hours were required to collect the precipitate from and measure the fluorescence of the samples used to determine the precision of the method. This required the processing of ten samples - one reagent blank, one sample containing 20 μg of  $I^-$ , one

sample containing 100  $\mu\text{g}$  of  $\text{I}^-$  and seven replicates containing 50  $\mu\text{g}$  of  $\text{I}^-$ . The  $\text{I}^-$  was recovered from a 1% KCl solution in this instance.

The method has been applied to the determination of iodide in water samples taken from a batholith in eastern Manitoba, Canada.

#### 4. ACKNOWLEDGEMENTS

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TABLE 1

COMPOSITION OF AECL REFERENCE GROUNDWATER (8)

Element	Concentration (mg/L)	
Na	8.55	± 0.33
K	2.78	± 0.06
Ca	10.6	± 0.4
Mg	4.30	± 0.07
Cl	12.9	± 0.4
F	0.202	± 0.003
NO <sub>3</sub>	0.732	± 0.012
SO <sub>4</sub>	0.044	± 0.015
Alkalinity calculated as HCO <sub>3</sub> <sup>-</sup>	84	± 2

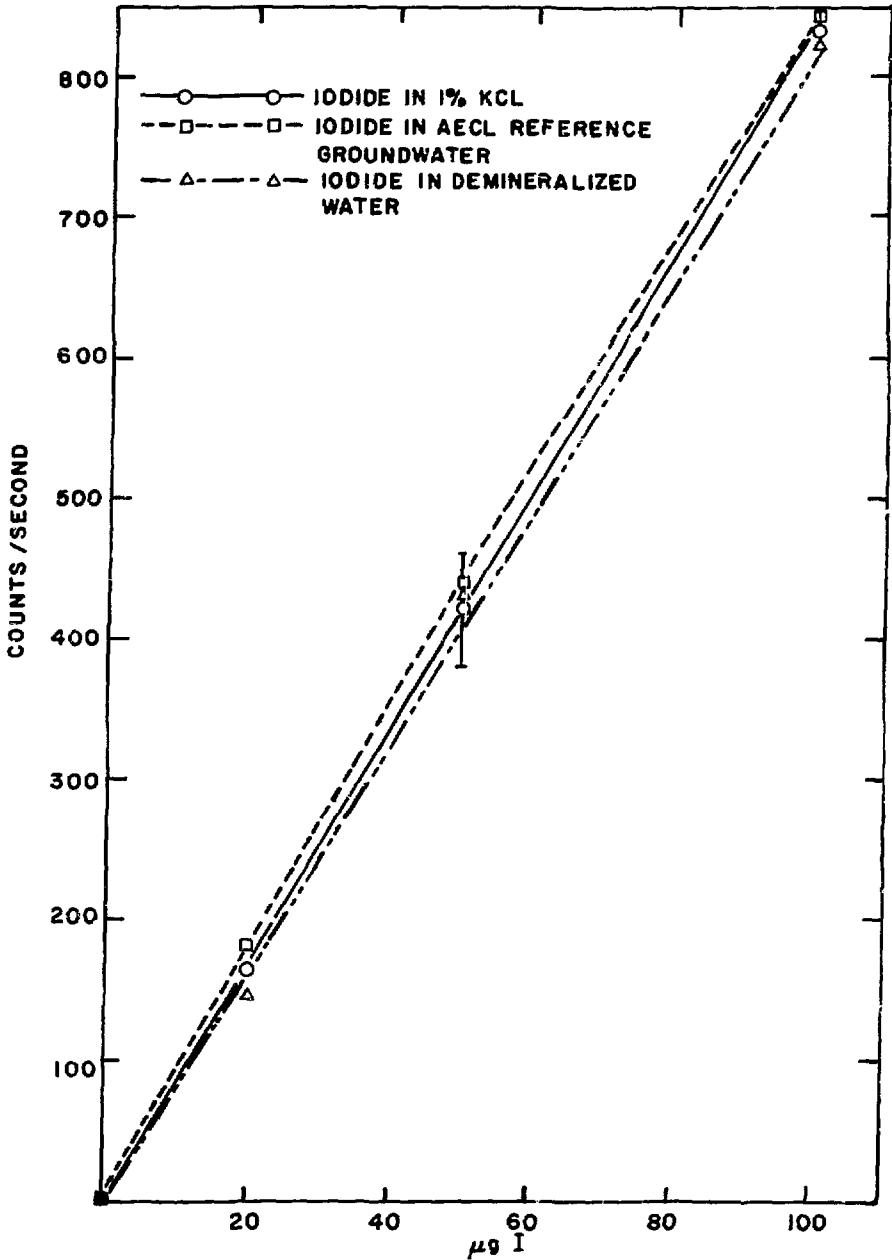


Figure 1: Response to Iodide in Media of Interest

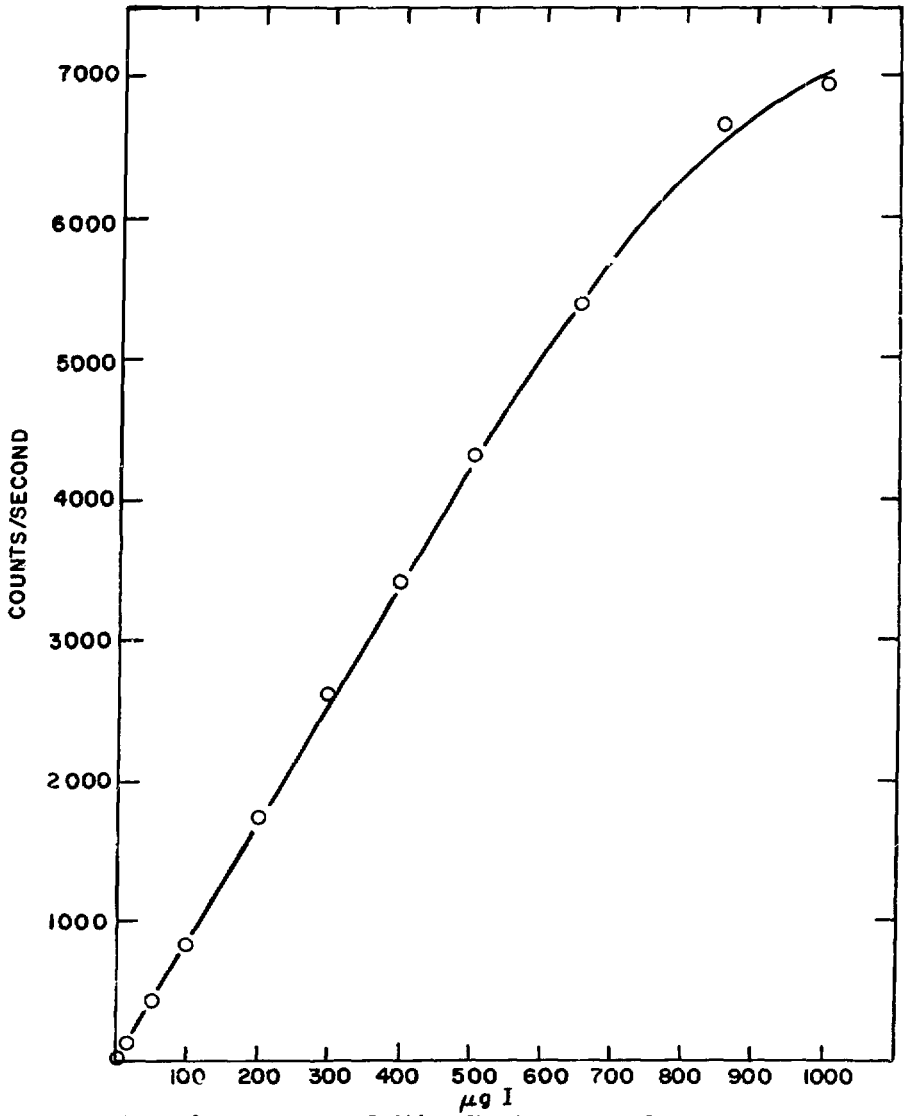


Figure 2: Response to Iodide, Showing Range of Linear Response

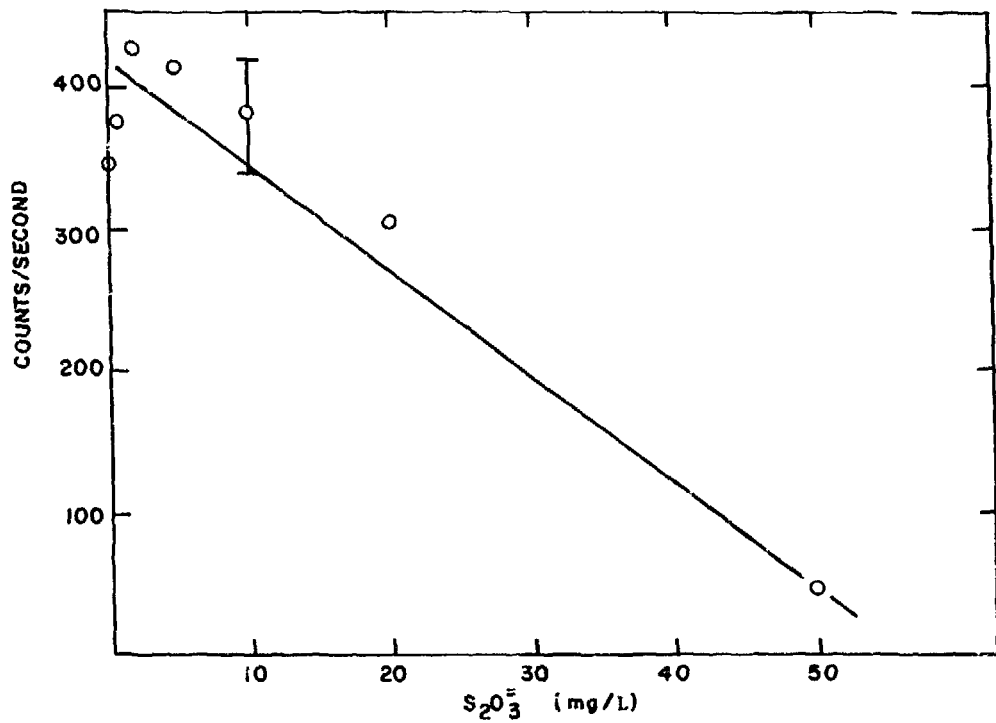


FIGURE 3 EFFECT OF THIOSULFATE ON THE RESPONSE TO 50 µg OF IODIDE



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