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Journal of Chromatography A, 850 (1999) 137–141

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Determination of total chromium in phosphate rocks by ion chromatography

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Abstract

Chromium(VI) is one of seven elements which is classified in the fertilizer industry as being harmful to plants and biological systems. Phosphate rocks represent the raw material for complex fertilizer production in the world. This paper investigates for the first time the determination of total chromium in phosphate rocks by ion chromatography. The developed analytical method involves the digestion of phosphate rocks with nitric acid followed by sample treatment of the resulting solution. The digestion solution obtained was treated with an oxidising agent (potassium peroxosulphate) to convert all chromium to the hexavalent state. The analytical method developed utilizes anion-exchange ion chromatography to achieve the separation and spectrophotometric post-column reaction for detection with diphenylcarbazide. The relative standard of deviation from analytical data comparison of six different phosphate rocks with atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry techniques, and cross-analysis data against an internationally certified phosphate rock standard were between 0.58 and 1.45%. Calibration curve between 0.2 and 0.9 $\mu\text{g/ml}$ was excellent, and the method has a detection limit for Cr(VI) of 0.05 ng. The developed method offers a fast, a reliable and an alternative procedure for the determination of total chromium in phosphate rock deposits by ion chromatography. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Phosphate rocks; Fertilizers; Chromium; Metal cations; Diphenylcarbazide

1. Introduction

Phosphate rocks are the raw material in the production of complex fertilizers in the world. Various phosphate rocks contain different concentration of micro elements of which chromium is a good example [1,2]. The range of concentration can vary significantly depending on the geological origin and the mining location of the phosphate rock.

Chromium is normally determined in the fertilizer industry by atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) [3,4], but recent literature re-

ports concerning these two analytical techniques indicate that the determination of chromium in fertilizer products was of intermediate quality due to spectral interferences [5,6].

Coupled ion chromatography (IC)–ICPC-AES is also reported for the determination of chromium [7]. Ion chromatography offers a highly specific method for the determination of Cr(VI) in drinking water by spectrophotometric post-column detection with diphenylcarbazide [8], where elution of Cr(VI) as its oxo-ion (CrO_4^{2-}) on an anion-exchange column was achieved. Since chromium can be present in phosphate rocks either as trivalent or hexavalent state [2], its total oxidation to the hexavalent state in a sample treatment procedure provides the basis for its total

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determination by ion chromatography in these raw materials. It was anticipated that the application of this highly specific method [8] to the determination of chromium in phosphate rock can have high potential of success.

An alternative ion chromatographic method for the analysis of total Cr in phosphate rocks was attempted. This method involves a simultaneous determination of Cr(III) and Cr(VI) on a single run by photometric detection of Cr(III) as its pyridinedicarboxylate (PDCA) complex and Cr(VI) via a post-column reaction with diphenylcarbazide both at 520 nm [9]. The negative results obtained from this method was due to the slow ligand exchange kinetics of the PDCA, and strong sample matrix interference where the Ca/Cr ratio is about 1500 [10].

Another ion chromatographic method [11] dealing with the analysis of chromium in geological samples was not attempted due to its sample preparation complex procedure, where fusion on aluminium oxide is necessary. The method has unacceptable baseline noise and it also involves the addition of sulphuric acid to the resulting fused solution, where in the case of phosphate rocks it would mean the precipitation of insoluble calcium sulphate.

At Norsk Hydro phosphate rocks are digested with nitric acid or sulphuric acid. Digestion with nitric acid is called the Odda process of fertilizers production [12].

In this work the determination of Cr(VI) in water samples by ion chromatography has been extended to include raw phosphate rocks used by Norsk Hydro, where total concentration of Cr in these production starting materials can be provided. The developed method relies on the total oxidation of Cr(III) to Cr(VI) with potassium peroxodisulphate in the presence of a silver catalyst [13], followed by Cr(VI) post-column detection with diphenylcarbazide.

2. Experimental

2.1. Instrumentation

A Dionex DX 300 (Dionex, Sunnyvale, CA, USA) equipped with a gradient pump system and a 10- μ l injection loop was used. Gilson auto-sampler model 221 (Gilson, France), and a UV150 Spectra-Physics

detector (Spectra-Physics, Santa Clara, CA, USA). Data handling was performed by a multichrom chromatography system (VG Instruments, UK). The column used was the anion-exchange functionality column IonPac AS7 (Dionex). The post-column reagent was introduced (0.5 ml/min) via a low-volume T-mixer with a nitrogen pressurized delivery system. The length of the reaction coil between the mixing the and the detector was 10 cm.

2.2. Reagents

Eluent, standard solutions and sample solutions were prepared with double-distilled water which has passed through a water purification system Milli-Q (Millipore, Waters Chromatography Division, Oslo, Norway). The eluent (1 ml/min) used to perform the elution is 25 mM ammonium sulphate and 100 mM ammonium hydroxide. The eluted metal ion was detected after spectrophotometric post-column reaction with diphenylcarbazide (2.0 mM, 10% methanol, 0.5 M sulphuric acid) at 530 nm. Standard solution for Cr(VI) 1000 μ g/ml was prepared by dissolving 0.283 g of potassium dichromate analytical-reagent grade (Merck, Germany), dried at 100°C for 1 h in 100 ml of water.

2.3. Sample preparation

Five grams of phosphate rock were digested with 50 ml of 7.2 M nitric acid by boiling for 15 min and made up to 20 ml mark with water in a 200-ml volumetric flask. A sample of 5 ml was taken from this 200-ml flask and placed in a 50-ml volumetric flask where 5 ml of 0.1 M solution of potassium peroxosulphate and 1 ml of 0.1 M solution of silver nitrate were added. The resulting solution was neutralized (pH 7–8) with 10 M sodium hydroxide solution and made up to 50 ml mark with water. The 50-ml volumetric flask was then placed in a oven at 80°C for 1 h, and then cooled to room temperature, filtered (0.2 μ m) and injected into the ion chromatograph.

3. Results and discussion

Diphenylcarbazide reacts with Cr(VI) ion eluted

as CrO_4^{2-} to produce a coloured complex which absorbs at 53 nm. Calibration curve for Cr(VI) ranging between 0.2 and 0.9 $\mu\text{g}/\text{ml}$ in water was obtained with excellent linearity. A similar calibration curve was also obtained from standard solution in matrix matching solution, however, with a slight reduction in retention time. The Cr(VI)

standard solution with matrix matching was prepared by digesting analytical-reagent grade calcium phosphate in nitric acid according to digestion procedure mentioned in Section 2.3. Fig. 1 shows Cr(VI) standard solution peaks with and without matrix matching. This reduction in retention time is due to the sample high concentration of nitrate and phos-

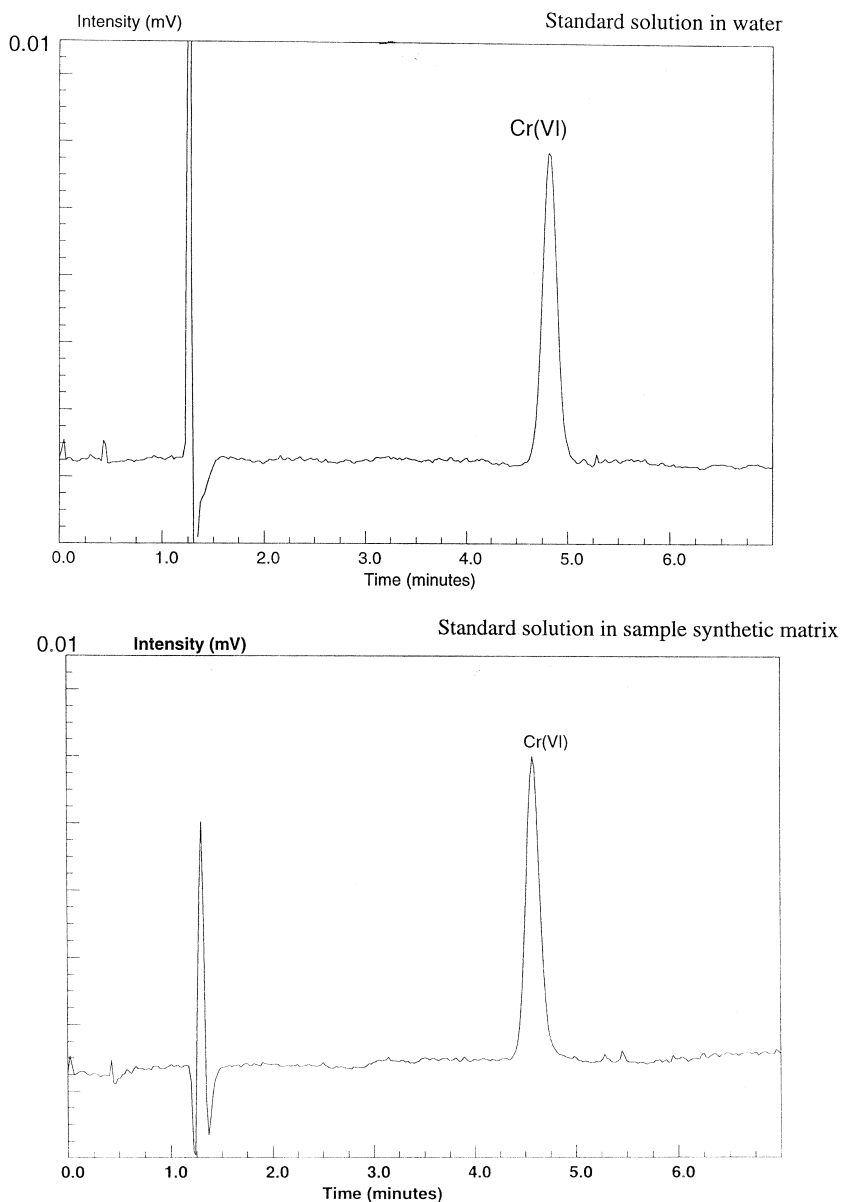


Fig. 1. Standard solution chromatograms (1 $\mu\text{g}/\text{ml}$) with and without sample matrix. IonPac AS7, 250 mM $(\text{NH}_4)_2\text{SO}_4$ and M NH_4OH (1 ml/min), detection with diphenylcarbazide.

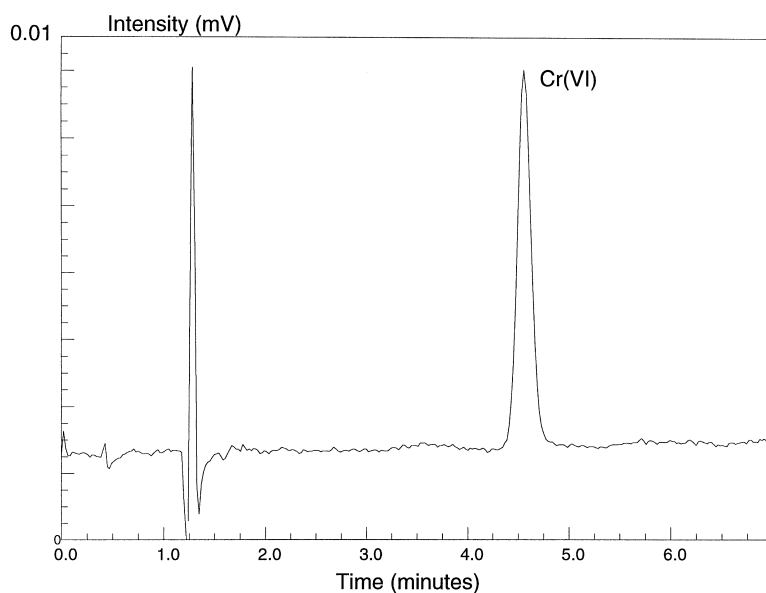


Fig. 2. Cr(VI) peak obtained from digestion of phosphate rock sample. Chromatographic conditions as in Fig. 1.

phate (10 000 $\mu\text{g}/\text{ml}$ and 500 $\mu\text{l}/\text{ml}$, respectively) in the sample, which occupy functional sites on the IonPac AS7 column and produces lower CrO_4^{2-} retention time. There was no post-column reaction between these high ions (NO_3^- and PO_4^{3-}) and diphenylcarbazide. This standard solutions matrix matching is necessary considering the natural composition of raw phosphate rocks [1,2]. Fig. 2 illustrates a typical Cr(VI) peak obtained from digested phosphate rock sample, which was prepared according with Section 2.3.

In order to demonstrate the accuracy of the developed IC method, the analysis of six different phosphate rocks were compared with two other analytical techniques namely AAS and ICP-AES. Table 1 lists the analytical data obtained from this

comparison. It is quite clear from Table 1 that this new IC method is in good agreement with the two other traditional methods of analysis.

The relative standard of deviation within the IC method which based on multiple injection ($n=5$) was calculated to be 1.56%. These repeatability experiments were conducted on samples with Cr(VI) concentration more than 10 times the detection limits. Detection limit for Cr(VI) based on three times the baseline noise was also calculated and found to be 0.05 ng. The method reliability was further confirmed by the analysis of a certified phosphate rock standard. This phosphate rock standard (Moroccan Phosphate rock, BCR No. 32) was obtained from the Bureau of Reference at the Commission of the European Communities, where

Table 1
Comparison analytical data of six phosphate rocks based on three parallel runs

Phosphate rock	Chromium ($\mu\text{g}/\text{g}$)		
	IC (RSD)	AAS	ICP-AES
Florida (USA) M4/90	49.38 (0.58%)	50.1	46.2
North Carolina (USA) M5/90	119.5 (1.45%)	117.7	108.5
Khourigba (Morocco) M1/96	241.1 (1.36%)	230.2	217.7
BouCraa (Morocco) M1/96	112.1(0.75%)	98.9	92.3
Togo (Africa) M24/86	111.2 (1.2%)	108.4	103.7
Jordan (Middle East) M9/90	71.2 (0.67%)	71.1	66.8

the certified value for total Cr is 257 $\mu\text{g}/\text{kg}$ (± 16 $\mu\text{g}/\text{g}$). The found value for total Cr by this developed method was 254 $\mu\text{g}/\text{g}$, with an RSD of 1.3% based on three complete parallel runs. This excellent agreement with the certified international standard further verifies the developed method accuracy and applicability.

4. Conclusion

The analysis of Cr(VI) by ion chromatography in water samples has been extended to the determination of total chromium in raw phosphate rock. The method is based on the total conversion of chromium(III) if present, to Cr(VI) by oxidation with potassium peroxosulphate, and subsequent detection with diphenylcarbazide. Excellent calibration curves, relative standard of deviation and repeatability studies were obtained. This IC method was proven by cross-comparison with two traditional analytical techniques and by verifying a certified phosphate rock standard. The developed method offers a fast, a reliable and an alternative procedure for the determination of total chromium in phosphate rock deposits by ion chromatography.

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