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Journal of Chromatography A, 739 (1996) 131–137

JOURNAL OF CHROMATOGRAPHY A

Application of ion chromatography to the analysis of high-purity CdTe

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Abstract

Ion chromatography is widely used in different fields of analytical chemistry and there is an extensive literature dealing with it, but not many papers describe the application of ion chromatography to the analysis of high-purity materials. A matter of topical interest in this field is the determination of impurity or dopant elements in the high-purity semiconductor compounds of $A^{II}B^{VI}$ type (CdTe) with detection limits from 10^{-4}% to 10^{-6}%. In order to eliminate the matrix effects and to reduce the detection limits, methods of concentration are commonly used; ion chromatography has been proved successful to separate impurities in the presence of large amounts of micro- and macro-components without any preconcentration and/or pre-separation steps. The proposed procedure deals with the ion chromatographic determination of chlorine, sulphur, selenium and phosphorus using a NaOH eluent, iron and copper using a PDCA eluent, lead, cobalt, zinc and nickel using an oxalate eluent. Detection limits range between 1 and $3\ 10^{-5}$% and calibration curves were found to be linear up to three orders of magnitude higher.The clear sample solutions were injected directly on to an ion chromatograph equipped both with a conductivity detector, for the determination of chloride, sulphate, selenate and phosphate ions, and a post-column membrane reactor and variable-wavelength UV–Vis detector, for the determination of iron, copper, lead, cobalt, zinc, nickel (and cadmium, if required). Ion chromatographic responses were compared to graphite furnace atomic absorption spectrometry and results were found to be in good agreement (±5%).

Keywords: Metal cations; Inorganic anions; UV photolyis; Semiconductors

1. Introduction

Most of the actual applications of cadmium telluride, like IR imaging in electro–optical devices, show the necessity of using high-resistivity (10^8–10^9 Ω cm) semi-insulating single crystals with an extended zone refining purification in order to remove a great part of the background impurities, together with chemical compensation by the appropriate element.

While theoretical calculations provide evidence that the limit of resistivity obtained by chemical and physical purification of CdTe is about 10^8 Ω cm, practically it is difficult to overcome 10^4 Ω cm: the decrease in the electric characteristics being attributed to the presence of carriers with different ionisation states and signs in the forbidden band gap of the material. Fig. 1 shows the energy levels diagram in CdTe forbidden band gap.

For chemical compensation, common donors were

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0021-9673/96/$15.00
PII S0021-9673(96)00220-8

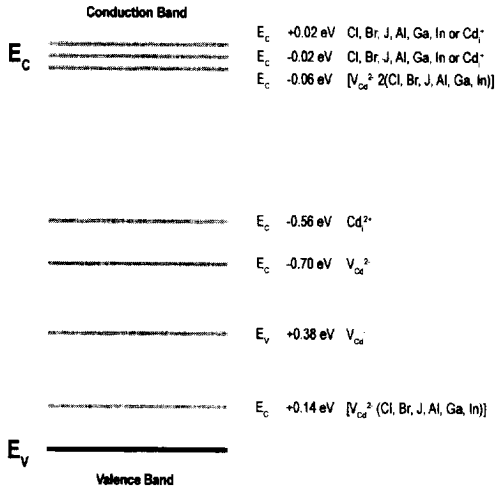

Fig. 1. Energy levels diagram in CdTe band gap.

considered both in group III elements, substitutive to Cd sites, and in group VII (halogen) elements, substitutive to Te sites. In addition complementary compensations by elements like Zn, Cu, Ag and Au are reported in literature. So it is of topical interest to determine impurity/compensation elements in high-purity CdTe with detection limits from 10^{-4} to 10^{-6}% (w/w) and different techniques have been employed [3,4] including neutron activation analysis [5], secondary ion [6,7] or spark source mass spectrometry [8], voltammetry [9], and graphite furnace atomic absorption spectrometry [10]. Most of these techniques are based on sample pre-treatments involving the additions of reagents and a lot of sample manipulations, while other require very expensive equipment and highly skilled personnel.

Not many papers describe the application of ion chromatography to the analysis of high-purity materials despite its capabilities in the separation of impurities in the presence of large amounts of the main component and of micro- and macro-components with close properties being well known [11]. Ion chromatography seems to be one of the most effective and simple techniques to determine both cationic as well as anionic species owing to its high sensitivity, rapidity and ease of operation coupled with the advantage of simultaneous determinations.

This paper presents a simple and accurate procedure for the dissolution of CdTe by oxidative UV photolysis and an ion chromatographic method that allows the simultaneous evaluation of chloride, sulphate, selenate and phosphate with a sodium hydroxide gradient and, with post-column spectrophotometric detection, of iron and copper using PDCA eluent and lead, cobalt, zinc, nickel and cadmium, if required, using an oxalic acid eluent.

2. Experimental

2.1. Reagents and standards

Sodium hydrogencarbonate, sodium acetate, oxalic acid, lithium hydroxide, 2-dimethylaminoethanol, 4-(2-pyridylazo)-resorcinol monosodium salt (PAR) and pyridine-2,6-dicarboxylic acid (PDCA) were chromatographic grade (Novachimica, Milan, Italy), hydrogen peroxide (30% m/m, without stabiliser), ammonium hydroxide (30%), sodium hydroxide, glacial acetic acid and nitric acid (70%) were Erbatron electronic grade (Carlo Erba Reagenti, Milan, Italy) while ammonium dihydrogenphosphate and magnesium nitrate were ACS reagent grade. 2 *M* ammonium acetate (pH=5.5) was chelation grade (Dionex, Sunnyvale, CA, USA). Ultrapure water with conductivity <0.1 μS (DI water) was obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

Working standards were prepared daily by diluting Carlo Erba Reagenti Normex atomic absorption standards (1.000 g/l) or by dissolving the required Carlo Erba Reagenti analytical-grade reagents.

Quartz test tubes and all glassware were cleaned in concentrated nitric acid and carefully washed with DI water. Normal precautions for trace analysis were observed throughout.

2.2. Eluent and post-column reagent solutions

A 50 m*M* and a 200 m*M* sodium hydroxide solution were used as chromatographic eluent for gradient separation of anions as summarised in Table 1.

For the analysis of iron(III) and copper(II), a mixture of 6 m*M* PDCA, 50 m*M* acetic acid and 50 m*M* sodium acetate (pH=4.6) was used as the eluent. A mixture of 50 m*M* oxalic acid and 95 m*M*

Table 1
Ion chromatographic conditions

	Anions	Fe, Cu, (Cd)	Pb, (Cd), Co, Zn, Ni
Column	IonPac AG10+AS10	IonPac CG5+CS5	IonPac CG5+CS5
Eluent	50 m*M* NaOH (0 to 10′) 143 m*M* NaOH (30 to 51′)	6 m*M* PDCA 50 m*M* CH_3COOH 50 m*M* CH_3COONa (pH 4.6)	50 m*M* Oxalic acid 95 m*M* LiOH (pH 4.8)
Eluent flow-rate	1.0 ml/min	1.0 ml/min	1.0 ml/min
Injection volume	15 μl	150 μl	150 μl
Detection	Suppressed conductivity	Visible absorbance	Visible absorbance
Suppressor	ASRS	–	–
Controller	Position 2 (100 mA)	–	–
Post-column	–	0.3 m*M* PAR	0.3 m*M* PAR
Reagent		1 *M* 2–dimethylaminoethanol 0.5 *M* NH_4OH 0.5 *M* $NaHCO_3$	1 *M* 2-dimethylaminoethanol 0.5 *M* NH_4OH 0.5 *M* $NaHCO_3$
PCR flow-rate	–	0.5 ml/min	0.5 ml/min
Wavelength	–	520 nm	520 nm

Table 2
Graphite Furnace Atomic Absorption Spectrometric conditions

Elements	Wavelength (nm)	Temperatures (°C)		Matrix modifier
		Pre-treatment	Atomisation	
Zn	213.9	700	1800	0.006 mg $Mg(NO_3)_2$
(Cd)	228.8	900	1600	0.2 mg $NH_4H_2PO_4$+0.01 mg $Mg(NO_3)_2$
Ni	232.0	1400	2500	0.05 mg $Mg(NO_3)_2$
Co	242.5	1400	2600	0.05 mg $Mg(NO_3)_2$
Fe	248.3	1400	2400	0.05 mg $Mg(NO_3)_2$
Pb	283.3	900	1800	0.2 mg $NH_4H_2PO_4$+0.01 mg $Mg(NO_3)_2$
Cu	324.8	800	2300	–

lithium hydroxide (pH=4.8) was employed for the determination of lead(II), cobalt(II), zinc(II) and nickel(II). The post-column reagent used with both eluents for cationic analysis was 0.3 m*M* PAR dissolved in 1 *M* 2-dimethylaminoethanol, 0.5 *M* ammonium hydroxide and 0.5 *M* sodium hydrogencarbonate.

2.3. Instrumentation

A laboratory mill (Spex, Edison, NJ, USA), fitted with an agate cell, was the standard apparatus used to prepare the samples. Finely ground semiconductor samples were subjected to UV photolysis in a Metrohm (Herisau, Switzerland) 705 UV digester equipped with a 500 W high-pressure mercury lamp. The temperature of the samples was maintained at 85±5°C with the help of a combined air/water cooling system.

Chromatographic analyses were performed on a metal-free Dionex DX-300 ion chromatograph equipped with an AGP gradient pump, an IonPac AG10 guard column and an IonPac AS10 anion separator column, an ASRS anion self-regenerating suppressor, an IonPac CG5 guard column and an IonPac CS5 cation separator column, a Post-column Pneumatic Controller for post column reagent addition, a CDM-III conductivity detector and a DSA UV–Vis multiple-wavelength detector. All the chromatographic conditions are listed in Table 1.

Table 3
Recovery and detection limit of different elements using ion chromatography

	Element[1]							
	Pb	Zn	Fe	Cu	Cl	$S-SO_4$	$Se-SeO_4$	$P-PO_4$
Added	0.010	0.050	0.010	0.010	0.050	0.050	1.00	0.050
Found	0.009	0.053	0.011	0.011	0.052	0.047	0.87	0.050
% recovery	90	106	110	110	104	94	87	100
Added	0.10	1.00	0.10	0.10	0.50	0.50	10.0	0.50
Found	0.11	0.95	0.11	0.09	0.51	0.50	10.3	0.52
% recovery	110	95	110	90	102	100	103	104
Added	0.50	100	1.00	0.50	5.00	1.00	25.0	1.00
Found	0.48	96.4	1.03	0.49	5.02	0.99	24.8	1.01
% recovery	96	96	103	98	100	99	99	101
Added	1.00	500	10.0	5.00	25.0	5.00	50.0	5.00
Found	1.03	505	9.94	5.06	24.9	5.02	49.9	5.01
% recovery	103	101	99	101	100	100	100	100
Detection limit[2]	0.005	0.005	0.005	0.002	0.010	0.030	0.030	0.035

[1] Values in mg/l of analysed solution.
[2] L.O.D. calculated as 3σ+average noise.

All measurements were made at room temperature and in all cases, injection of the sample was done at least in triplicate. All the samples were filtered through 0.45 μm filter.

Data manipulation and the operation of all components in the system were controlled by AI-450 Dionex chromatographic software interfaced via an ACI-2 Advanced Computer Interface to a 80386 based computer (Epson, Sesto S. Giovanni, Italy).

A Varian (Mulgrave, Victoria, Australia) Spectra 400 atomic absorption spectrometer, equipped with a GTA 96 graphite tube atomiser, was used for comparison purposes. The spectrometric working conditions are listed in Table 2. Each analysis called for 20 μl of sample, and 10 μl of the matrix modifier was added if necessary, according to Table 2. It was then carried out on a pyro/platform tube in an argon stream, with a slit of 1 nm (for Zn), 0.5 nm (for Cu and Pb) or 0.2 nm (for Ni, Co and Fe) and by using the resonance lines reported in Table 2. Only Pb was analysed in an uncoated tube.

The results were obtained by computerised graphic evaluation of the standard addition method, taking into account the matrix modifier dilution when requested.

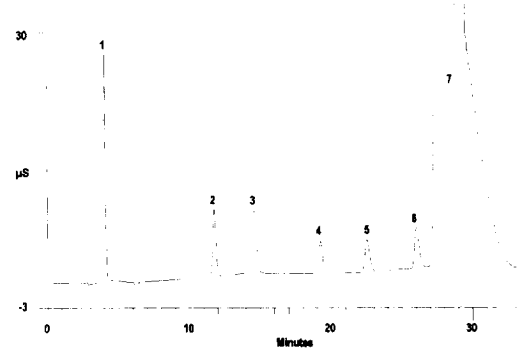

Fig. 2. Chromatographic behaviour of anions present in the solution resulting from the oxidative UV photolysis CdTe dissolution (chromatographic conditions as in Table 1). Peaks: 1. F^-, 2. Cl^-, 3. NO_2^-, 4. SO_4^{2-}, 5. SeO_4^{2-}, 6. PO_4^{3-} and 7. NO_3^-.

2.4. Sample preparation

After etching with 0.5 *M* nitric acid in order to remove the surface layer, the sample was washed in DI running water and dried in pure nitrogen flow, then it was finely powdered in a mill fitted with an agate cell.

A sample of 15 to 70 mg of finely ground semiconductor were weighted in a quartz tube and 50 μl of concentrated nitric acid followed by 0.5 ml of H_2O_2 (30%) was added. The quartz tube was closed with a conical PTFE stopper tapered to a point. The

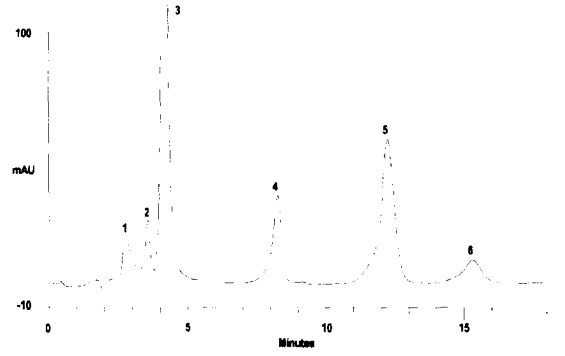

Fig. 3. Chromatographic behaviour, using oxalic acid eluent, of cations present in the solution resulting from the oxidative UV photolysis CdTe dissolution (chromatographic conditions as in Table 1). Peaks: 1. Pb^{2+}, 2. Cu^{2+}, 3. Cd^{2+}, 4. Co^{2+}, 5. Zn^{2+} and 6. Ni^{2+}.

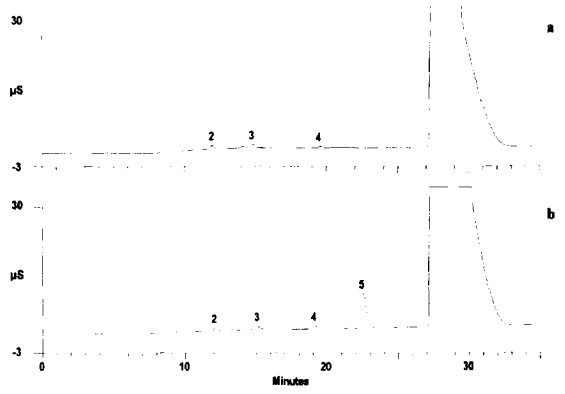

Fig. 5. Determination of anions in uncompensated CdTe (chromatographic conditions as in Table 1). (a) reagents blank; (b) sample: 5. SeO_4^{2-} (20.8 mg/l).

stopper acted as a cooling finger, prevented solution loss and also protected the sample against contamination. The sample was subjected to UV photolysis in a digester equipped with a high-pressure mercury lamp (500 W) for 60–120 min as described in previous papers [1,2]. The temperature of the sample did not exceed 85±5°C by means of a combined air/water cooling system. The matrix was oxidised and metal and non-metal quantitization remained unaffected by UV radiation, except for nitrate (added), iodide and manganese. The photolysis has decisive advantages compared with other sample dissolution methods, due to the simple procedure and the minimal reagent addition requirement resulting in minimal contamination. After cooling, its volume was made up to 10 ml with DI water and analysed.

When the PDCA eluent was used, before making up the volume with DI water, 500 µl of 2 *M* ammonium acetate was added to keep the sample pH into the range between 5 and 6.

3. Results and discussion

Because CdTe standards did not exist, the detection limits and linear ranges were determined by spiking samples of different types with various

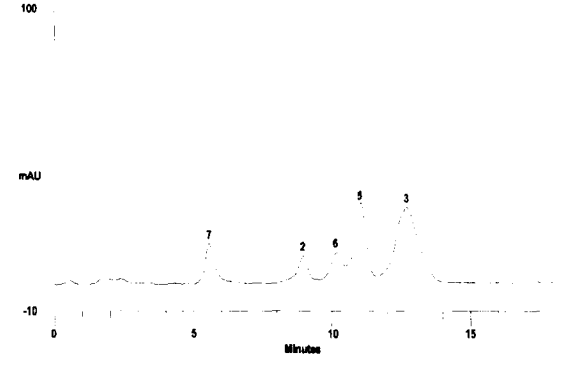

Fig. 4. Chromatographic behaviour, using PDCA eluent, of cations present in the solution resulting from the oxidative UV photolysis CdTe dissolution (chromatographic conditions as in Table 1). Peaks: 7. Fe^{3+}, 2. Cu^{2+}, 3. Cd^{2+}, 5. Zn^{2+} and 6. Ni^{2+}.

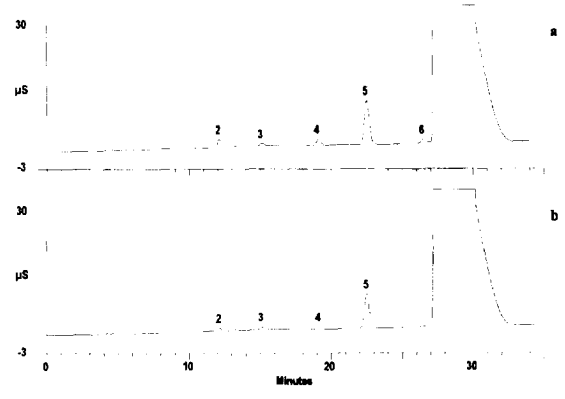

Fig. 6. Determination of anions in uncompensated CdTe (chromatographic conditions as in Table 1). (a) CdTe before purification; 2. Cl^- (0.8 mg/l), 4. SO_4^{2-} (1.2 mg/l), 5. SeO_4^{2-} (27.5 mg/l), 6. PO_4^{3-} (0.4 mg/l); (b) CdTe after purification; 5. SeO_4^{2-} (20.8 mg/l).

amounts of the determined species, subjecting them to oxidative UV photolysis for one to two hours and analysing them by means of the proposed procedure. Some data are summarised in Table 3 while in Figs. 2–4 their chromatographic behaviour is reported. Fig. 3 shows that, when using oxalic acid eluent, copper is too close to the cadmium matrix excess to be determined at low levels and similarly when using PDCA eluent, as shown in Fig. 4, nickel and zinc are too close to the cadmium matrix excess, which explains the need of two different eluents for cations determination.

The results show that oxidative UV photolysis, in the reported conditions, did not affect the recovery of the reported elements. Hydrogen peroxide provided free OH* radicals which accelerated the sample decomposition without interfering with analytes, because the decomposition products were only water and oxygen. A minimum amount of nitric acid addition was required to contribute to sample dissolution via NO* radicals and to prevent any metal oxide formation. The UV radiation helped sample dissolution by promoting ions into the semiconductor conduction band, increasing its conductivity and exciting a more active charge transfer. In this way, the energy supplied by UV radiation improved sample dissolution by shortening the time and minimising reagent addition.

The proposed method was applied to the analysis of different CdTe samples and Fig. 5a and b, Fig. 6a and b, Fig. 7a and b, and Fig. 8a and b show chromatograms of a sample in different purification steps compared to their respective blanks.

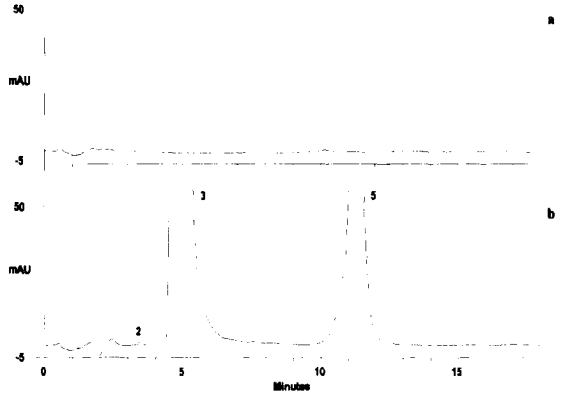

Fig. 7. Determination of cations, using oxalic acid eluent, in Zn compensated CdTe (chromatographic conditions as in Table 1). (a) reagents blank; (b) sample: 2. Cu^{2+} (21 μg/l), 5. Zn^{2+} (14.4 mg/l, sample solution diluted 1:10).

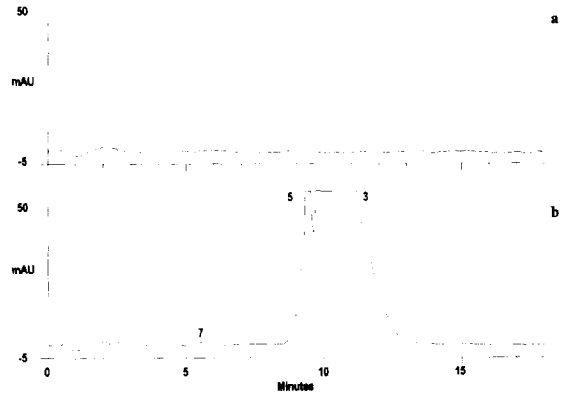

Fig. 8. Determination of cations, using PDCA acid eluent, in Zn compensated CdTe (chromatographic conditions as in Table 1). (a) reagents blank; (b) sample: 7. Fe^{3+} (11 μg/l).

For Pb, Zn, Fe, and Cu, in absence of standards, the results were compared to those obtained by graphite furnace atomic absorption spectrometry (GFAAS). The same comparison was not possible for the other elements because of the lack in alternative common techniques sensitivity requirements. Table 4 shows that results are in good agreement.

Table 4
Elements determined in different types of electronic grade CdTe samples

Elements	Analytical technique	CdTe Samples[1]			
		A	B	C	D
Pb	IC	<0.05	<0.05	<0.05	<0.05
	GFAAS	<0.05	<0.05	<0.05	<0.05
Zn	IC	<0.05	<0.05	8340	1200
	GFAAS	<0.05	<0.05	8263	1216
Fe	IC	0.06	0.09	153	526
	GFAAS	0.07	0.09	149	521
Cu	IC	0.05	<0.02	12.4	13.1
	GFAAS	0.05	<0.02	13.0	13.6
Cl	IC	1013	975	<0.1	<0.1
$S-SO_4$	IC	0.3	0.3	0.5	0.4
$Se-SeO_4$	IC	1645	1803	2012	1766
$P-PO_4$	IC	0.8	0.7	1.1	0.9

[1] Values in μg/g. RSD% ±10 (range 0.02–1 μg/g); ±4 (range 1–10000 μg/g).

No interference of the species usually found in CdTe was found, the only drawbacks being the bromide co-elution with nitrate and the UV radiation influence over iodide, thus making impossible their determination.

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