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High-Purity Zinc, Cadmium, Tellurium, Indium and Gallium: Preparation and Analysis

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Abstract

We describe simple and efficient methods of profound purification of cadmium, zinc and tellurium by vacuum distillation, indium and gallium – by the electrolysis of their chlorides. The results are characterized.

INTRODUCTION

The problem connected with profound purification and characterization of the substances that are used for the synthesis of compounds $A^{II}B^{VI}$ and $A^{III}B^{V}$ remains urgent. Because of this, the advantages of methods providing efficient purification using rather simple and cheap equipment are evident. As far as the characterization of purified substance is concerned, since the effect of every impurity on the target properties of the material often remains unknown, multielement methods remain preferable because they provide the lowest possible detection limits for several tens of impurities simultaneously.

EXPERIMENTAL

In order to obtain pure cadmium, zinc and tellurium, low-melting elements with high vapour pressure at low temperatures, we used vacuum distillation in the presence of their oxides [1, 2]. The scheme of setup is shown in Fig. 1. The set-up includes a tube made of pure quartz which is about 1 m long and 60 mm in diameter. The tube has three zones: the first for evaporation, the second for condensation, and the third zone is free. The first two zones are heated with resistor furnaces. The load mass is 1.5–1.8 kg, the yield of pure metal is about 1–1.1 kg. The final stage of the process is directed crystallization in the condensation zone under conditions providing the growth of single crystal.

Low melting points of indium, gallium and their chlorides allow to use electrolysis for their purification. The scheme of electrolyzer (made of pure quartz) is shown in Fig. 2. Anhydrous indium and gallium chlorides used as electrolytes were obtained by the interaction of pure metal with ammonium chloride and additionally purified by distillation. The eletrolyzer is placed in a vertical electrical furnace. The productivity of the electrolyzer is about 1 kg of pure metal per day.

RESULTS AND DISCUSSION

The characterization of high-purity metals is provided by the combination of chemical spectral methods, mass spectral ones and atomic

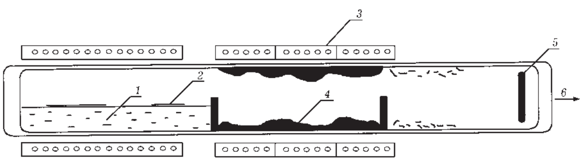

Fig. 1. The scheme of set-up for the purification of zinc, cadmium and tellurium by distillation: *1* – initial metal, *2* – oxide film, *3* – three-sectional resistance furnace, *4* – condensate; *5* – screen, *6* – to the roughing pump.

TABLE 1
Results of zinc purification

Impurity	Mass fraction, %		
	in initial zinc	after 1st distillation	after 2nd distillation
Ag	$1 \cdot 10^{-4}$	$2 \cdot 10^{-6}$	n. d. ($5 \cdot 10^{-8}$)
Al	$3 \cdot 10^{-3}$	$1 \cdot 10^{-6}$	$5 \cdot 10^{-7}$
As	$5 \cdot 10^{-5}$	n. d. ($5 \cdot 10^{-6}$)	n. d. ($5 \cdot 10^{-6}$)
Bi	$5 \cdot 10^{-5}$	n. d. ($4 \cdot 10^{-7}$)	n. d. ($4 \cdot 10^{-6}$)
Ca	$1 \cdot 10^{-4}$	$5 \cdot 10^{-6}$	$5 \cdot 10^{-7}$
Cu	$2 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	$5 \cdot 10^{-7}$
Fe	$2 \cdot 10^{-4}$	$6 \cdot 10^{-7}$	$6 \cdot 10^{-7}$
Mg	$4 \cdot 10^{-5}$	n. d. ($6 \cdot 10^{-7}$)	n. d. ($4 \cdot 10^{-7}$)
Mn	$1 \cdot 10^{-5}$	n. d. ($2 \cdot 10^{-7}$)	n. d. ($8 \cdot 10^{-8}$)
Ni	$1 \cdot 10^{-4}$	$1 \cdot 10^{-6}$	n. d. ($4 \cdot 10^{-7}$)
Pb	$1 \cdot 10^{-4}$	n. d. ($6 \cdot 10^{-7}$)	n. d. ($6 \cdot 10^{-7}$)
Sb	$1 \cdot 10^{-4}$	n. d. ($1 \cdot 10^{-6}$)	n. d. ($1 \cdot 10^{-6}$)
Sn	$1 \cdot 10^{-3}$	$1 \cdot 10^{-6}$	n. d. ($5 \cdot 10^{-7}$)
Σ_{13}	$6.9 \cdot 10^{-3}$	$< 2.2 \cdot 10^{-5}$	$< 1 \cdot 10^{-5}$

Notes. 1. All impurities discovered in initial zinc are included. 2. Here and in Tables 2, 3: n. d. – impurity not discovered; detection limit is given in parentheses.

TABLE 2
Results of cadmium purification

Impurity	Mass fraction, %		
	in initial cadmium	after 1st distillation	after 2nd distillation
Mg	$2 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	n. d. ($2 \cdot 10^{-7}$)
Ca	$5 \cdot 10^{-5}$	n. d. ($7 \cdot 10^{-7}$)	n. d. ($7 \cdot 10^{-7}$)
Al	$4 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	n. d. ($3 \cdot 10^{-7}$)
Sn	$1 \cdot 10^{-5}$	n. d. ($4 \cdot 10^{-7}$)	n. d. ($1 \cdot 10^{-7}$)
Fe	$1 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	n. d. ($3 \cdot 10^{-7}$)
Cu	$1 \cdot 10^{-2}$	$1 \cdot 10^{-6}$	n. d. ($5 \cdot 10^{-8}$)
Ag	$3 \cdot 10^{-3}$	$7 \cdot 10^{-8}$	n. d. ($2 \cdot 10^{-8}$)
Co	$4 \cdot 10^{-5}$	n. d. ($5 \cdot 10^{-7}$)	n. d. ($1 \cdot 10^{-7}$)
Ni	$3 \cdot 10^{-3}$	n. d. ($1 \cdot 10^{-7}$)	n. d. ($1 \cdot 10^{-7}$)
Pb	$5 \cdot 10^{-3}$	n. d. ($4 \cdot 10^{-7}$)	n. d. ($1 \cdot 10^{-7}$)
Sb	$5 \cdot 10^{-5}$	n. d. ($6 \cdot 10^{-7}$)	n. d. ($6 \cdot 10^{-7}$)
Bi	$5 \cdot 10^{-5}$	n. d. ($6 \cdot 10^{-7}$)	n. d. ($6 \cdot 10^{-8}$)
Zn	$4 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	n. d. ($5 \cdot 10^{-7}$)
Mn	n. d. ($1 \cdot 10^{-6}$)	$2 \cdot 10^{-7}$	n. d. ($5 \cdot 10^{-8}$)

Note. Impurities not discovered in purified cadmium: Be, Ga, In, Mn, Au, Rh, ($n \cdot 10^{-8}$); Ba, Sc, V, Ti, Cr, Mo, Y, Pd, Pt, Pb, Rb, Cs ($n \cdot 10^{-7}$); B, La, Ge, Zr, W, Ir, Re, Os, Hg, Hf, Tl, As, Se, Te, Li, P, Cl, F, Br, I ($n \cdot 10^{-6}$); Si, Na, K, O, N, C ($1 \cdot 10^{-5}$).

TABLE 3
Results of tellurium purification

Impurity	Mass fraction, %	Impurity	Mass fraction, %
Cu	n. d. ($5 \cdot 10^{-8}$)	Cr	n. d. ($1 \cdot 10^{-7}$)
Ag	n. d. ($1 \cdot 10^{-8}$)	Sn	n. d. ($2 \cdot 10^{-7}$)
Mn	n. d. ($1 \cdot 10^{-8}$)	Au	n. d. ($1 \cdot 10^{-7}$)
In	n. d. ($3 \cdot 10^{-8}$)	Sb	n. d. ($4 \cdot 10^{-7}$)
Be	n. d. ($1 \cdot 10^{-8}$)	Mo	n. d. ($2 \cdot 10^{-7}$)
Bi	n. d. ($5 \cdot 10^{-8}$)	V	n. d. ($1 \cdot 10^{-7}$)
Ga	n. d. ($5 \cdot 10^{-8}$)	Pt	n. d. ($5 \cdot 10^{-7}$)
Co	n. d. ($5 \cdot 10^{-8}$)	Pd	n. d. ($5 \cdot 10^{-7}$)
Fe	n. d. ($2 \cdot 10^{-7}$)	Ti	n. d. ($1 \cdot 10^{-7}$)
Al	n. d. ($5 \cdot 10^{-7}$)	Ca	n. d. ($1 \cdot 10^{-6}$)
Mg	n. d. ($5 \cdot 10^{-7}$)	La	n. d. ($1 \cdot 10^{-6}$)
Ni	n. d. ($2 \cdot 10^{-7}$)	Cd	n. d. ($5 \cdot 10^{-7}$)
Pb	n. d. ($1 \cdot 10^{-7}$)	Zn	n. d. ($5 \cdot 10^{-7}$)

Note. $100\ \% - \sum^{26} \geq 99.99999\ \%$.

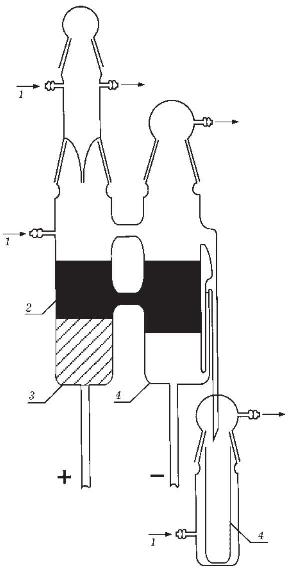

Fig. 2. The scheme of electrolyzer for the purification of indium and gallium: *1* – argon, *2* – electrolyte ($MeCl_n$), *3* – initial metal, *4* – purified metal.

absorption used to determine the composition of impurvities [3–9]. Every sample can be analysed for the content of about 70 impurities; however, as a rule, 20–30 impurities are controlled as standards. One of the most important parts in the set of methods belongs to atomic emission spectral analysis with preliminary concentrating of the impurities by distilling the main component of the sample [5, 6, 9]. The advantage of distillation as compared to widely used extraction of the main component is the possibility to use larger weighed portion, smaller number of analysis operations and reduced reagents consumption.

Tables 1–3 show the results of zinc, cadmium and tellurium purification. One can see that the proposed technology provides the material with the purity not worse than 99.99999 %.

Gallium and tellurium purification by electrolysis has been tested for the preparation of 99.99999 grade from the wastes of electronics production. The sum of 24 impurities content (Cu, Ag, Mn, Be, Bi, Ga, Co, Fe, Al, Mg, Ni, Pb, Cr, Sn, Au, Sb, Mo, V, Pt, Pd, Ti, Ca, La, Cd) in indium purified by electrolysis is not more than $9.6 \cdot 10^{-6}$ % and 24 impurities in gallium (Cu, Ag, Mn, In, Be, Bi, Co, Fe, Al, Mg, Ni, Pb, Cr, Sn, Au, Sb, Mo, V, Pt, Pd, Ti, Ca, La, Cd) account for not more than $9.4 \cdot 10^{-6}$ %. Indium and cadmium samples are presented at the Collection of Pure Substances Exhibition in Nizhniy Novgorod. Indium was recognized in 1994 as the purest sample among those produced in Russia. In 1997, cadmium was recognized among the best home samples presented at the Exhibition before 1997.

CONCLUSION

Thus, simple and rather cheap technologies based on vacuum distillation (for the purification of zinc, cadmium, tellurium) and electrolysis of the corresponding chlorides (for indium and gallium purification) allow to obtain the substances of 7N qualification with the productivity of about 1 kg per day.

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