

Extraction of Trace Metal Impurities from High-Purity Inorganic Salts

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Received January 1, 2014

Abstract—Extraction of trace metal impurities from a matrix followed by the determination of the mass concentration of the impurities by means of atomic emission spectrometry was studied. The method allows determination of the concentrations of such contaminants as Fe, V, Mn, Cu, Ni, and Co at the level of 10^{-5} – 10^{-7} wt %.

DOI: 10.1134/S1070363215100436

INTRODUCTION

The application field of high-purity substances is constantly growing. High-purity substances are applied in all high-tech fields, such as micro- and optoelectronics, optics and fiber optic communication lines, nanotechnological systems, and high-temperature construction ceramic products.

The increasing quality requirements to such products pose more and more complicated tasks for analytical chemistry. The most comprehensive information about high-purity substances at the atomic and molecular levels can be gained by means of information-rich analytical techniques [1].

For substances used in optical glass making, of particular importance is to know the concentrations of the impurities of color-imparting metals, such as Fe, V, Mn, Cu, Cr, Ni, and Co.

The main goal we set ourselves in the present work was to develop methods for the determination of trace metal impurities in ammonium nitrate, sodium chloride, and lithium and sodium fluorides at the level of 10^{-5} – 10^{-7} %.

Theory. Atomic emission spectrometry with inductively coupled plasma atomization (ICP–AES) is the most popular express high-sensitivity method of identification and quantification of trace metals in

gaseous, liquid, and solid substances, including high-purity ones. This method is widely applied in different fields of science and technics for industrial production control, search for and processing of minerals, in biological, medical, and environmental research, etc. An important advantage of atomic emission spectrometry over other optical spectral, as well as many chemical and physicochemical methods of analysis is that it offers the possibility of express and highly precise quantification of a great number of elements over a wide range of concentrations, using a small sample volume. At the same time, this method is not sensitive enough for trace analysis, and not infrequently additional concentration steps should be included into the sample preparation procedure [2]. The relative detection limit can be decreased by artificially reducing the effect of the matrix. One of the most common approaches is the concentration of impurities, which makes possible separation the impurities from the matrix or replacement of the matrix. Therewith, the error associated with sampling errors are much reduced, and this allows one to operate with more representative samples .

Concentration is made possible by the fact that macro- and microcomponents of a sample have different chemical and physical properties: solubility, sorption capacity, boiling and sublimation points, and size, charge, or mass of the ions. Not infrequently such differences are created artificially, using oxidation, reduction, masking, or other methods.

The inclusion of the concentration stage makes the entire analysis more time- and labor-consuming, requires additional purification of reagents, increases analyte losses and may lead to sample contamination, sometimes decreases the number of analytes which can be determined in a group method, and decreases the metrological characteristics of the method. However, the detection limits of impurities can be much decreased.

Extraction is one of the most promising concentration technique in the analysis of high-purity substances, waters, biological samples, etc. Extraction methods are suitable both for absolute and relative concentration. Two concentration modes are possible: extraction of impurity elements or extraction of matrix elements.

The advantages of extraction are as follows:

- well-developed theoretical basis;
- wide range of available extractants and extraction reagents, which provides the possibility to select the most suitable ones;
- easy to perform; high efficiency; good compatibility with various detection techniques [3].

The extraction systems used for the extraction of trace metal impurities are quite diverse and include coordinately unsolvated neutral compounds (AsI_3), ionic associates, coordinately solvated neutral complexes with tributyl phosphate (TBP) ($\text{ScCl}_3 \times \text{TBP}$), metal halide and pseudometal halide acids (HTiCl_4), and chelates.

Chelates are the most widely used class of compounds used for extractive concentration of trace elements.

Quite common reagents for group concentration of heavy and transition metal trace impurities are dithiocarbamates, such as sodium diethyl dithiocarbamate (Na-DDC), ammonium pyrrolidine dithiocarbamate (NH_4 -DDC), and hexamethylene ammonium hexamethylene dithiocarbamate (HMA-HMDC). These reagents are accessible, have a wide range of action, and are easy to purify. The partition coefficients R of metal complexes between water and these reagents are high enough for trace impurities to be extracted from large ($40\text{--}80\text{ cm}^3$) volumes of water.

The extraction of impurities from real samples is associated with matrix effects. Thus, certain salts, for example, halides of alkali metals (especially Li and Na), accelerate equilibration in the extractive concentration of a Fe chelate. Masking agents introduced

to prevent hydrolysis of the matrix not infrequently shift the optimum extraction range of impurities, which should be taken into account in the development of the concentration method. The data in the handbooks are mostly related to extraction from pure solutions. Studying Fe, V, Mn, Cu, Ni, and Co extraction as dithiocarbamate chelates from various solvents with chloroform showed that the composition of the aqueous phase strongly affects the extraction efficiency. As shown in [4], Cu, Ni, and Co are fairly efficiently extracted in the pH range 3–8 both in the presence and in the absence of complex-forming agents. The optimum extraction pH for Fe and Mn in tartrate and, especially, oxalate media shifts to the alkaline range by several pH units. Addition of phosphate ions increases the recovery of chromium and vanadium, as well as extends the extraction range. Dithiocarbamates have an essential drawback: they rapidly decompose in acidic aqueous media ($\text{pH} < 4$). However, even though diethyldithiocarbamic acid is an unstable compound and rapidly decomposes in acidic media, this process slows down as the decomposition products are accumulated in the aqueous phase, and this fact can be used in practice. The optimum pH range for the extraction of many elements is 4.5–6.5, and only Mn is well extracted at pH 7–9. Diethyldithiocarbamate metal complexes are commonly extracted with chloroform, carbon tetrachlorides, and other water immiscible solvents [4].

The procedure of extractive concentration, applied in most analytical laboratories, is the so-called batch extraction performed in separatory funnels, tubes with ground stoppers, or conical flasks. Here, if the extractant volume is fixed, the R value the higher, the higher is the number of operations, and, consequently, the smaller volume of the organic phase in each operation [5].

A convenient approach to accelerating equilibration and increasing the concentration factors of impurities provides homogeneous or single-phase extraction. In this method, the extractant or reagent is an organic compound readily miscible with water, and, after the complex formation has been complete, the aqueous and organic phases are separated artificially. Thus, Mo is extracted with propylenecarboxylic acid which mixes with water at 70°C , whereas on cooling the system separates into layers, and the organic phase contains up to 97% of Mo. Isopropanol and acetone are active extractants, but they mix with water in any proportions. However, such mixtures can be separated

into two phases by means of a salting-out agent (NaCl, CaCl₂, or MgCl₂), and, therewith, the organic phase contains the extracted substance [6].

An approach to analysis of high-purity substances, which allows the quantity of the reagent to be reduced 10 times, has been described [7]: The reagent is added to the system in a water-miscible solvent, the solution is left to stand for a while and heated, if necessary, after which the resulting complexes and excess reagent are extracted with a small volume of an appropriate solvent that functions as an active additive favoring extraction of the unsaturated complexes. This approach is especially convenient, because in this case no salting-out reagents which adversely affect the blank values are needed.

In view of the aforesaid, we performed optimization of extractive sample preparation for the determination of trace metals impurities in metal salts, such as sodium chloride and lithium and sodium fluorides, at the level of 10^{-5} – 10^{-7} wt %.

EXPERIMENTAL

Reagents, solutions, and auxiliary materials. Ammonium nitrate and sodium chloride were purified by recrystallization from aqueous solutions.

Lithium and sodium fluorides were prepared by exchange reactions from special purity hydroxides and HF.

Solutions of the analytes with the concentrations of 1 mg/cm³ were prepared according to State Standard 4212-76.

Aqueous ammonia of special purity (State Standard 24147-80), nitric acid of special purity (State Standard 11125-78), hydrochloric acid of special purity (State Standard 14262-77), and hydrofluoric acid of ultrahigh purity (UHP 27-5; Technical Specifications 6-09-3401-88) were distilled without boiling in Berghof BSB-939-IR Teflon apparatus (Germany).

Distilled water (State Standard 6709-72) was additionally purified using a Sartorius Arium 611 water purification system (Germany).

Hydrogen peroxide (State Standard 177-88) was used as received.

An aqueous solution of nitric (3.5 vol %) and hydrochloric (15 vol %) acids was prepared (Solution 0).

The extraction system contained 100 mL of chloroform and 40 mL of acetone. Both solvents were preliminarily purified by distillation.

Solutions containing 2% of extractants (Na-DDC, NH₄-DDC, and HMA-HMDC) were prepared in ethanol.

Cylinder-stored argon of high-purity (State Standard 10157-79) was used.

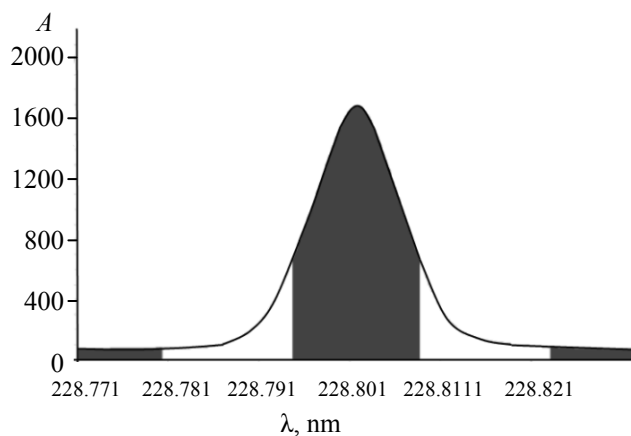
Instruments and equipment. A Thermo Fisher Scientific iCAP 6300 duo ICP-OES spectrometer; a BAVp-01-Laminar-C-1,2 (class II, type B2) laminar cabinet (air quality Class 5 – ISO according to State Standard R ISO 14644-1-2002).

Preparation of solutions of impurities for introduction to salt solutions and calibration of the spectrometer. Single-element solutions of each impurity (Fe, V, Mn, Cu, Ni, and Co) with the concentration 1 mg/mL were prepared according to State Standard 4212-76. These solutions were mixed and diluted to obtain multielement solutions with the concentrations of each component 10, 100, and 1000 µg/L, using Solution 0 as a diluent.

Sample preparation. Trace metal ions are generally present in salts in the form of cationic and anionic complexes or inclusion compounds which may prevent efficient extraction [5]. To exclude this effect, reduce the effect of the traces of organic and inorganic reagents applied for the preparation and purification of the target analyte, and obtain an active form of the trace metals, the latter were oxidized by treatment of the sample with HNO₃ doped with H₂O₂ followed by heating. For milder acid digestion the samples were prewetted with water, which allowed us to reduce analyte losses. The impurities were introduced before dissolution of the samples by adding to them required volumes of the multielement solutions.

Ammonium nitrate and sodium chloride samples were prepared as follows. A 2.00-g sample of salt was placed into a quartz beaker, after which 1 mL of deionized water, 2 mL of conc. HNO₃, and 1 mL of conc. H₂O₂ were added, and the mixture was heated until gas evolution was no longer observed. Deionized water, 20 mL, was then added, the pH of the resulting solution was brought to 5.5 with 10% ammonia, and the solution was diluted to the final volume of 40 mL.

Metal fluoride samples were prepared as follows [7, 8]. A 2.00-g sample of salt was placed into a glassy carbon beaker, after which 1 mL of distilled water and



Cadmium peak in the center of the subarray.

4 mL of concentrated sulfuric acid were added. The solution was heated on a heating plate until sulfuric acid began to evaporate, 2 mL of deionized water was added, and the mixture was heated again until sulfuric acid began to evaporate. This operation was repeated 3 times to completely remove fluoride ions from the solution. Excess acid was neutralized with 10% ammonia to pH 5.5, and then the solution was diluted to 40 mL.

The solution was transferred into a separatory funnel and 1 mL of a 2% extractant solution and 5 mL of the extraction mixture were added. After 5-min extraction the organic phase was transferred into a dry quartz dish. An additional 0.5 mL of a 2% solution of Na-DDC and 5 mL of the extraction mixture were added to the separatory funnel. After 5-min extraction the organic phase was transferred to the same quartz dish.

The combined phase was transferred with caution into a Teflon dish so that water droplets remained on the walls of the quartz dish. The organic phase was evaporated to dryness on an IR heater, not allowing the solution to boil, and the dry residue was treated with 0.5 mL of conc. HNO_3 and 0.05 mL of conc. H_2O_2 , after which the solution was evaporated to dryness on a heating plate. Concentrated nitric acid, 0.05 mL, was added to the residue, and the walls of the crucible were rinsed with 1 cm³ of Solution 0. With each concentration, no less than 3 runs were performed. Blank samples were prepared in the same way but in the absence of the analytes. The concentrates were then analyzed by ICP-OES spectrometry.

Algorithm of analysis. *a.* The atomic emission spectrometer is prepared according to the manual as follows:

- the optical system is purged with argon before turn on and continuously during operation at a flow rate of 2 dm³/min;
- the instrument is turned on, the spectral block is thermostated for 2 h;
- plasma is ignited, stabilization time 10 min;
- plasma discharge parameters: high-frequency generator power 1150 W, auxiliary gas flow rate 0.5 dm³/min, carrier gas flow rate 0.7 dm³/min;
- the optimum plasma region to be observed and the wavelength for each element are determined separately. The registered signal should look as a symmetrical peak in the center of the subarray (see figure).

Background is measured on the left and right of the peak and subtracted automatically by the software.

b. Calibration of the instrument:

- a reference solution (for example solution *a*) is injected into plasma;
- calibration solutions are then injected;
- using the algorithm in the manual, calibration plots are constructed as first-order polynomials and saved in the computer.
- the plots are retrieved during analysis; current conditions are accounted for by regular recalibration using one calibration solution.

As analyzed solutions are injected into plasma, the results of analysis are displayed on the monitor in required concentration units corrected for the concentration factors. The nebulizer is washed with Solution 0 after each sample.

Each sample is analyzed in triplicate, and the arithmetic mean of the three runs is taken as the result of analysis $\pm(10-15)$ % at the confidence probability $P = 0.95$.

RESULTS AND DISCUSSION

For clean blanks liquid reagents (water, acids, NH_4OH , organic solvents) are used, because their purity parameters are several orders of magnitude higher compared to solid substances. The acids and NH_4OH were additionally purified by isothermal distillation (sub-boiling). Only freshly distilled acids were used.

To prevent contamination of the analytes, all glassware is carefully prepared before analysis.

To reduce the effect of the traces of organic and inorganic reagents used in the synthesis and purification of the analytes, as well as to obtain an active form of trace metal impurities, the interfering impurities are oxidized by treatment of the samples with HNO₃ doped with H₂O₂, after which the solutions were evaporated to wet salts.

Before acid digestion of the analyzed product the sample is wetted with water to ensure milder digestion conditions to prevent losses of the analytes. In dissolving metal fluorides sulfuric acid was used as an expellent for fluorides.

To prevent emulsification which prevents the enrichment factor, because the organic phase mechanically entraps aqueous phase droplets, a special extractor for separatory funnels, designed to exclude dynamic liquid impingement followed by settlement of the organic phase in a dry quartz vessel after the organic phase has separated from the aqueous phase.

The main problem of extractive concentration in the analysis of ultrapure substances is to increase the recovery of the analyzed impurities under the provision that the matrix and impurities have been sufficiently completely separated from each other.

In developing optimum conditions for the extractive concentration of trace Fe, V, Mn, Cu, Ni, and Co impurities from ammonium nitrate, sodium chloride, and lithium and sodium fluoride solutions we made use of Na-DDC, NH₄-DDC, and HMA-HMDC. These compounds showed good results as extractants for individual and group extraction of trace heavy metals from various compounds, forming weakly polar hydrophobic complexes. The conditions for group concentration were optimized by a systematic study of the effect of the acidity of the initial solution, dithiocarbamate concentration, and composition of the extraction mixture on the recovery of each metal [6].

For complete extraction of the impurities into the organic phase we performed experiments to select a reagent suitable for these specific systems and optimum pH values for the aqueous phase. In the experiments we used model solutions with the concentration of each impurity (C_0) of 5×10^{-6} wt %. Reagents were introduced into the aqueous phase as ethanol solutions.

The recoveries of the impurities, obtained in these experiments, are listed in Table 1. None of the three reagents was able to concentrate after single extraction

Table 1. Dependence of R , %, of trace metal impurities on the nature of the reagent and the acidity of the aqueous phase

Reagent	pH	Mn	Fe	Ni	V	Cu	Co	Cr
Na-DDC	2	–	41	70	22	100	53	–
NH ₄ -DDC	2	–	60	70	25	100	66	–
HMA-HMDC	2	–	70	65	40	60	68	–
Na-DDC	5	97	92	88	96	100	91	91
NH ₄ -DDC	5	53	90	82	89	99	92	54
HMA-HMDC	5	65	81	76	64	93	79	51
Na-DDC	8	62	85	79	–	63	85	–
NH ₄ -DDC	8	72	80	52	70	62	64	37
HMA-HMDC	8	41	49	69	50	74	51	43

all the components of the group at pH = 2–3. The optimal pH value was 5–6.

Good results were obtained, when the complex formation and extraction stages were separated. To this end, the reagent was introduced into the aqueous phase dissolved in water-miscible solvent (ethanol). This approach allows one to considerably reduce the quantity of the reagent and, as the same time, create a high concentration of the latter in the aqueous phase.

For higher recoveries, 2–3 extraction runs are made, and the extracts are combined in a quartz dish. The extracts are evaporated in mild conditions (without boiling and not allowing the dry residue to overheat), for example, by using an IR heater; not meeting such requirements leads to considerable analyte losses due to sublimation of the chelates. The losses due to sorption on the dish walls can be avoided by rinsing the dish after the evaporation of the organic phase with a small volume of conc. HNO₃, as well as by using Teflon dishes. The recoveries of the impurities on evaporation of the chloroform extract in dishes from different materials and at different procedures of the preparation of the concentrate are listed in Table 2.

To optimize extraction conditions at a minimum number of operations, we performed a series of experiments using model solutions with $C_0 = 5 \times 10^{-6}$ wt % in each analyte. Reagents were introduced into the aqueous phase as ethanol solutions. None of the three reagents was able to concentrate after single extraction all the trace metals at pH = 2–3. The optimal pH value was 5–6.

Table 2. Dependence of R , %, of trace metal impurities on the material of the dish and the concentrate preparation procedure for the evaporation of the chloroform extract

Evaporation conditions	Impurity weight, mg	Fe	V	Mn	Cu	Cr	Ni	Co
In a quartz dish	0.2	13	40	50	50	40	36	40
	1.0	25	65	60	80	55	64	52
In a Teflon dish	0.2	70	72	95	100	75	100	100
	1.0	75	80	100	100	95	100	100
In a Teflon dish; the dry residue was dissolved in 0.05 mL of conc. HNO ₃	0.2	85	95	100	100	80	100	100
	1.0	89	87	100	100	92	100	100

In the analysis of ultrapure substances, when the concentration of impurities in their solutions is 10^{-6} wt % and lower, the problem that the impurity concentration affects the R value arises. As known, at concentrations of up to 10^{-4} wt %, the R value is almost independent on the concentration of the extracted element [6], but whether this is the fact, when the concentration of the latter is lower by 2–3 orders of magnitude, should be verified experimentally. To this end, we prepared model solutions with the starting impurity concentrations $C_0 < 1 \times 10^{-8}$ wt %, into which we introduced the impurities as typical solutions of inorganic compounds in quantities corresponding to the concentration range from 1×10^{-5} to 5×10^{-8} wt %. The resulting data showed that the R value remains constant up to the concentration 4×10^{-7} wt % and decreases to 50% and lower, when the concentration is decreased to 5×10^{-8} wt %. The recovery can be increased by increasing reagent concentration and making 2–3 extraction runs.

Solvents capable of complex formation should be used for extraction [6]. With this in mind, for the

Table 3. Recoveries of trace metal impurities for the extraction with different extractants from a sodium chloride solution (spiked concentration of each metal $1\text{--}10^{-6}$ wt %)

Analyte	Reagent		
	Na-DDC	NH ₄ -DDC	HMA-HMDC
Mn	0.9	0.8	0.6
Fe	1.1	0.7	1.1
Ni	0.9	0.7	0.8
V	0.8	0.9	0.6
Cu	1.0	1.2	0.9
Co	0.8	0.6	0.9
Cr	1.2	0.8	0.5

extraction of DDC complexes we used a mixture of acetone and chloroform, taking into account that acetone can form complexes with metals. At the same time, acetone is readily miscible both with water and with chloroform.

In the case of small volumes of the initial solution, the concentrate contains a large excess of the complex-forming reagent which, as a rule, is transferred into the extract, which affects the physicochemical properties of the concentrate. Therefore, the latter are better analyzed after mineralization and dissolution in water. A typical mineralization procedure was developed. The organic extracts are evaporated under an IR lamp in round-bottomed conical Teflon dishes, treated with 1 mL of HNO₃ doped with H₂O₂ to oxidize organic complexes, and the dry residue after evaporation is dissolved in 1 mL of Solution 0, thoroughly rinsing the walls. Further on the concentrate from the dish is directly injected into plasma. Solutions of the impurities in the HCl + HNO₃ mixture of the specified composition were used as calibration solutions. The error in the measurement of the analytical signal in such procedure was no larger than 15%.

The efficiency of the group extraction of the trace metals in focus with dithiocarbamates was estimated by the spike-and-recovery method. The results listed in Table 3 provide evidence for the group extraction of trace Fe, V, Mn, Cu, Ni, and Co impurities from the matrix solutions.

Ashing of NH₄-DDC and HMA-HMDC created serious difficulties in the ICP–OES analysis of the concentrates, which puts the value of these reagents in doubt, even though they exhibit good extraction characteristics.

Thus, the present research showed that Na-DDC is a suitable extractant for separation and concentration of trace metal impurities in the systems studied. A

typical scheme of extractive concentration of impurities of high-purity substances of different chemical nature is developed. The considered of sample preparation procedures involving dissolution of the sample, concentration of the impurities, and preparation of the concentrate for atomic emission analysis, make it possible to analyze, with low detection limits, metal trace impurities in salts, and also can be extended to such objects as oxides and composites applied in different fields of technology.

ACKNOWLEDGMENTS

The work was financially supported by the Ministry of Education and Science of the Russian Federation and fulfilled using the equipment of the "Research and Analytical Center of the State Research Institute of Chemical Reagents and Special Purity Chemical Substances Federal State Unitary Enterprise" Center for Collective Use.

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