

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Flame Spectrometry in Analysis of Refractory Oxide Single Crystals

T.V. Sheina and K.N. Belikov
*State Scientific Institution "Institute for Single Crystals"
of National Academy of Sciences
Ukraine*

1. Introduction

This chapter is devoted to the use of flame atomic-emission and atomic-absorption spectrometry techniques to determine the stoichiometric composition, as well as studying the regularities of distribution of impurities and dopants in single crystals based on refractory oxides used as active media for solid-state lasers (leucosapphire, ruby, yttrium-aluminium garnet), laser light modulators (strontium titanate), scintillation detectors (cadmium tungstate), solid electrolytes (β -alumina), medical implants (leucosapphire).

Growth of high quality single crystals requires not only adherence to specifications and the growing parameters but reliable methods of analytical control of their composition. Last years along with so-called F-centre forming elements, the increasing attention is given to alkali and alkali-earth impurities which also may cause worsening of quality of single crystals (Dobrovinskaya et al., 2007; Nagornaya et al., 2005; Tupitsyna et al., 2009).

Digestion of refractory oxide single crystals is one of the most complicated and important stage of the procedure of analysis. Condensed phosphoric acid is recommended as an effective reagent for sample preparation of single crystals of oxide compounds. For the rapid flame spectrometry determination of alkali metals and calcium impurities, procedures of the sample preparation of water extracts of α - and γ -forms of aluminum oxide, yttrium-aluminum garnet and magnesium-aluminates used as raw materials for single crystals growing are proposed. It is also shown the effectiveness of ultrasonic sample preparation technique followed by the direct determination of Co and Ni in suspensions of α - Al_2O_3 .

2. Phosphoric acid digestion of refractory oxide single crystals followed by flame spectrometry analysis

The most commonly used methods of digestion of sparingly soluble substances have a number of shortcomings. Alkali fusion techniques result in high blank values for alkali-earth elements and totally unsuitable for alkali elements determination. Heating of single crystals samples with different acid mixtures is time consuming and not always effective procedure even when autoclave digestion method is used (Foner, 1984; Haines, 1988; Homeier et al., 1988; Krasil'shchik et al., 1986; Morikava, 1987; Otruba, 1990). It is shown, that for the acid digestion of minerals and oxides condensed phosphoric acid can be successfully applied (Bock, 1979; Hannaker, 1984; Mizoguchi, 1978). It can be obtained by dissolving of P_2O_5 in

75 % orthophosphoric acid. Also, upon heating orthophosphoric acid, condensation of the phosphoric groups can be induced by driving off the water formed from condensation (Mizoguchi, 1978; Zolotovitskaya et al., 1984). Sometimes, dehydration is performed at the reduced pressure and temperature 260...300 °C (Corbridge, 1990). Condensation of orthophosphoric acid leads to forming the mix of polyphosphoric acids which are strong complexing agents having high dissolving ability (Zolotovitskaya et al., 1984, 1997; Trachevskii et al. 1996).

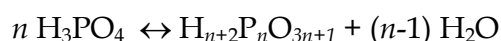
In this section the main results on application of condensed phosphoric acid for the digestion of wide range of compounds are presented. Among the investigated materials were aluminium oxide single crystals and fusion mixtures; magnesium aluminium spinel doped with Fe, Ni, Co, V, Ti; yttrium aluminium garnet; gallium scandium gadolinium garnet doped with Nd; cadmium tungstate; strontium titanate and other functional materials.

2.1 Thermally activated acid-base transformations in the system “condensed phosphoric acid – oxide material”

The composition of the polyacids obtained after heating of an orthophosphoric acid, the mechanism of solvent action of polyphosphoric acids as well as the composition of complex compounds formed during digestion of analysed materials in condensed phosphoric acid has been studied by heteronuclear NMR spectroscopy (Trachevskii et al., 1996). The NMR spectra (^{31}P , ^{17}O , ^{27}Al , ^{113}Cd) of liquid and solid samples were recorded on Bruker CXP-200 spectrometer using single and multipulse sequences as well as magic angle spinning techniques.

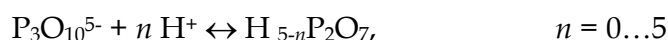
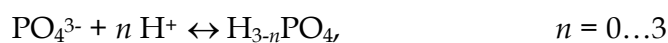
Heating-up to 400 °C of 75 % orthophosphoric acid leads to driving off the water and to forming linear polyphosphoric acids. Identification of the obtained substances was performed using ^{31}P NMR spectroscopy of water solutions of corresponding salts as well as water solutions derived from melts partly neutralized by ammonia.

In the investigated temperature range (20...400 °C) a set of processes of orthophosphoric acid transformations can be expressed by the following equation:



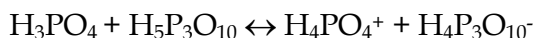
where $n = 1 \dots 12$.

From the point of view of prediction of reactivity of dissolvent the effect of upfield shift of signals in ^{31}P NMR spectra, corresponding to consecutive thermal generation of polyphosphatic homologues (with $n=2, 3, 4$) (Trachevskii et al., 1996) is important. The analogous trend of change of signals was observed at shift of acid-base equilibriums towards augmentation of protonation of anions:



With driving off the water, the equilibrium $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$ is shifting towards formation of molecular form H_3PO_4 . At these conditions the strongest base

remaining in system is a orthophosphoric acid. The nearest homologues have more strongly pronounced acid function and the following equilibriums take place:



Thus, along with consumption of H_3PO_4 in condensation processes the yield of the molecular di - and triphosphate forms increases. Also, formation of the highest, more acidic homologues leads to augmentation of probability of formation H_4PO_4^+ .

The obtained data allows us to consider that the solvent action factors are: (1) acid-base transformations of O^{2-} anion in the reaction with H_4PO_4^+ cation with formation of the following forms where acid function increases in the order: $\text{O}^{2-} < \text{OH}^- < \text{H}_2\text{O} < \text{H}_3\text{O}^+$, (2) complexing properties of di - and triphosphate anions. A complex formation with other polyphosphates is less probable owing to a smaller yield of these compounds and high viscosity of medium.

The following empirical characteristics describing processes of digestion of different compounds in condensed phosphoric acid were obtained: (a) conditional solubility (mass of dissolved material per 1 cm^3 of H_3PO_4); (b) optimum temperature of dissolution (t_{opt} , $^{\circ}\text{C}$); (c) average dissolution rate at fixed temperature (V , g min^{-1}); (d) degree of dissolution (α , %). Kinetics of dissolving $\alpha\text{-Al}_2\text{O}_3$ and CdWO_4 was investigated. A mixture of 0.3 g of $\alpha\text{-Al}_2\text{O}_3$ and 10 ml of H_3PO_4 or 0.6 g of CdWO_4 and 5 ml of H_3PO_4 was kept at fixed temperature for a definite time. Then, after centrifugation, concentration of Al in solution was determined by flame atomic absorption spectrometry and concentrations of Cd and W were determined by X-ray fluorescence spectrometry (Mirenskaya et al., 1994).

Kinetic curves of dissolving Al_2O_3 and CdWO_4 (Fig. 1) are s-shaped where initial and finite parts correspond to low dissolution rate which is limited by evaporation of water and decreasing of content of solid phase in reaction volume, respectively. A middle part of curves is linear and corresponds to the maximum dissolution rate (97 % of CdWO_4 and 80-85 % of Al_2O_3 go in solution) when simultaneous processes of acid-base transformations, polycondensation of H_3PO_4 and forming of metal phosphate complexes are take place.

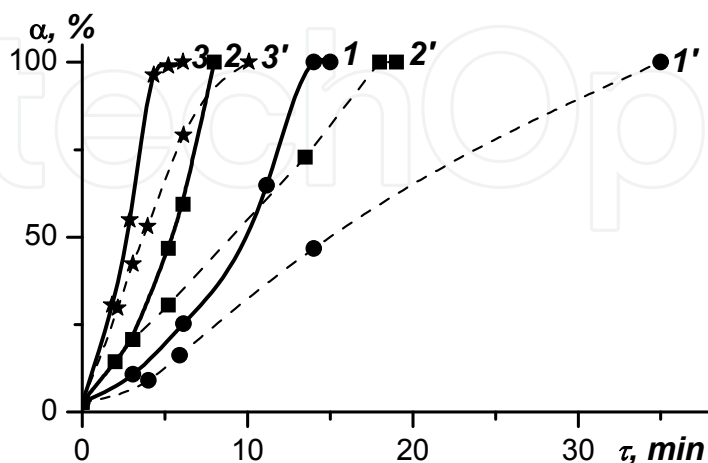


Fig. 1. Kinetics of dissolving Al_2O_3 (1' - 3') and CdWO_4 (1 - 3) in condensed phosphoric acid: 215 $^{\circ}\text{C}$ (1, 1'), 270 $^{\circ}\text{C}$ (2, 2'), 330 $^{\circ}\text{C}$ (3, 3').

In Fig. 2 dependences of dissolution rate of different fusion mixtures and single crystals on temperature are presented. The mass of samples was 0.05...2.00 g and volume of H_3PO_3 was 10 ml for Al_2O_3 or TiO_2 and 5 ml for WO_3 . Dramatic increase in dissolution rate is observed at 210...270 °C for charge and at 250...300 °C for single crystals. Optimum values of temperature for dissolving of fusion mixtures and single crystals were 270 and 300 °C, respectively. It was unreasonable to dissolve such materials at higher temperatures due to formation of sparingly soluble vitreous products. The obtained data were used for optimization of sample preparation procedures of some oxide materials (Table 1).

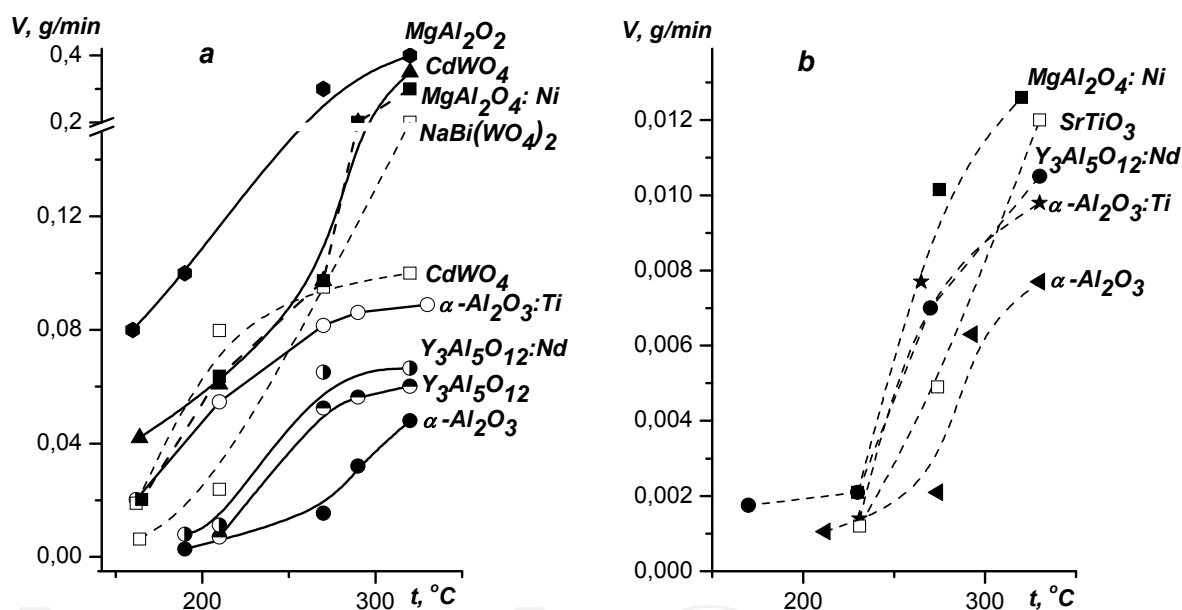


Fig. 2. Dependence of dissolution rate of different fusion mixtures (—) and single crystals (- -) on temperature

NMR-spectroscopy data (Trachevskii et al., 1996) has allowed us to explain high hydrolytic stability of phosphate decomposition products. Analysis of ^{31}P NMR spectra for the system of $K_2WO_4 - H_3PO_4$ has shown that after dilution there are significant amounts of diphosphate anions and their complexes with tungsten in solutions. Presence of specified diphosphate complexes as well as solvable orthophosphate complexes is the main reason of stability of diluted solutions. Obviously, similar processes cause the same behavior of other oxide materials studied in this work.

Material	Sample mass, g	Temperature, °C	Digestion time, minutes	Conditional solubility, g cm ⁻³
α -Al ₂ O ₃ charge	0.3...0.4	270	16	0.05
α -Al ₂ O ₃ single crystal	0.15	290...300	30	0.016
α -Al ₂ O ₃ :Ti charge	0.3	270	13	0.09
α -Al ₂ O ₃ :Ti single crystal	0.2	300	25	0.02
<i>m</i> Al ₂ O ₃ <i>n</i> Y ₂ O ₃ charge	0.3...0.4	270	11	0.07
<i>m</i> Al ₂ O ₃ <i>n</i> Y ₂ O ₃ <i>k</i> Nd ₂ O ₃ charge	0.3...0.5	270	10	0.09
<i>m</i> Al ₂ O ₃ <i>n</i> Y ₂ O ₃ <i>k</i> Nd ₂ O ₃ single crystal	0.2...0.3	300...320	20	0.05
<i>m</i> Al ₂ O ₃ <i>n</i> MgO charge	0.3...0.6	270	5	0.20
<i>m</i> Al ₂ O ₃ <i>n</i> MgO:Ni charge	0.3	270	6	0.20
<i>m</i> Al ₂ O ₃ <i>n</i> MgO:Ni single crystal	0.1	270	18	0.03
SrTiO ₃ charge	0.1	330	9	0.010
CdWO ₄ charge	0.6...0.8	265	9	> 0.40
CdWO ₄ single crystal	0.6...0.8	270	15	0.40
NaBi(WO ₄) ₂ single crystal	0.4...0.8	300...330	8	> 0.40

Table 1. Optimum conditions of digestion of some single crystals and raw materials in condensed phosphoric acid

2.2 Flame spectrophotometric analysis of phosphate solutions of refractory oxides

The combination of a highly effective digestion technique with flame atomic-emission (FAES) and atomic-absorption (FAAS) analysis of the phosphate solutions was used for the determination of Na, K, Ca in α -Al₂O₃; Ca in SrTiO₃; Na, K, Ca, Mg in CdWO₄; dopants Li, Na, Mg in β -Al₂O₃; Nd in yttrium aluminium garnet; Ti, V, Fe, Co, Ni in corundum; Li, Rb, Cs, Sr, Ba in CdWO₄; a stoichiometric composition of garnets $(n-x)Y_2O_3$ xNd_2O_3 mAl_2O_3 and MgO kAl_2O_3 where *n* can vary from 1 to 3, *m* and *k* - from 1 to 5, *x* - from 0 to 0,2.

Flame spectrometry measurements were performed on a spectrophotometer "Saturn" (Ukraine) with use of acetylene-air, propane-butane-nitrous oxide and acetylene-nitrous oxide gas mixtures. The processes taking place during flame atomization of materials and excitation are well studied (Havezov et al., 1983; Haswell, 1991; Hill, 2005; L'vov et al., 1975; Magyar, 1987; Welz, 1999). However, application of flame spectrometry in analysis of solutions of the complex composition especially containing metal phosphate complexes, demands to study of influence of various factors on absorption and emission signals of analytes. Most essential of them are the main composition of solution and conditions of atomization of material in a flame. The last depends on the chosen gas mixture, a fuel/oxidant ratio, zone of photometric observations. The numerous data available in the literature on this problem are ambiguous.

2.2.1 Effects of redox characteristics of the flame and the height of the burner on analytical signals

The redox characteristics of a flame defined by the fuel/oxidant ratio were estimated visually, basing on the height of the inner cone (*l*, mm) which was changed over a range from 1 to 5 for acetylene-air, propane-butane-nitrous oxide flames and from 1 to 40 for

acetylene-nitrous oxide flame. It was considered that acetylene-air and propane-butane-nitrous oxide flames were oxidative, stoichiometrical or reducing when l was equal to 1...2, 3...4 and 5...6, respectively. The corresponding values for the acetylene-nitrous oxide flame were 1...2, 2...35 and 40...45.

In order to investigate effect of redox characteristics of the flame on analytical signals they were recorded at different distances above the burner orifice while l value was constant. It has been found that analytical signals of all elements of interest depend on redox characteristics of a flame. Most distinctly these dependences are appeared for the metals forming hardly dissociated compounds (alkali-earth and rare-earth elements, Al) even when a high-temperature flame is used (Maitra, 1987; Pupyshev. et al., 1990).

As an example, in Fig. 3 dependences of analytical signals of Al and Y on the height of the inner cone of the flame are presented.

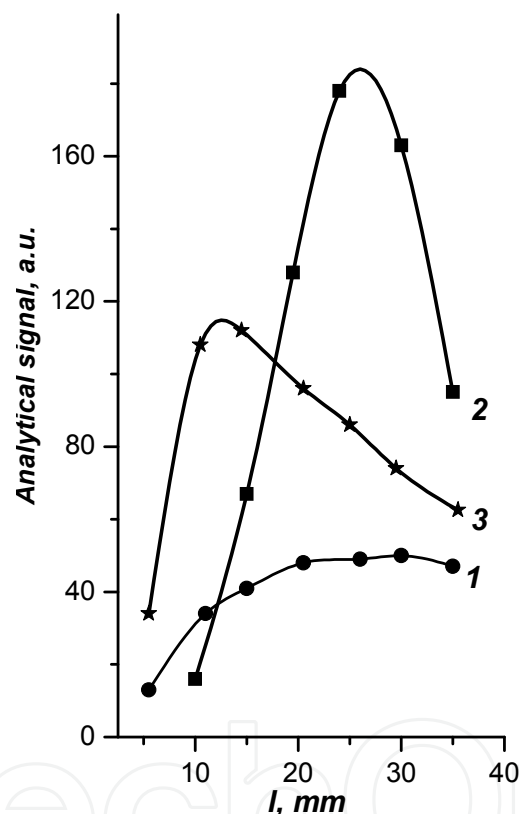


Fig. 3. Dependence of absorption signals of Al (1) and Y (2) and an emission signal of Al (3) in phosphate solutions of $Y_3Al_5O_{12}$ on the inner cone of the flame (l , mm)

It can be seen that at determination of these elements, especially by atomic-emission method, it is necessary to select a fuel/oxidant ratio very carefully. For alkali-earth metals, Mg and metals of subgroup Fe composition of gas mixture is less critical, however also is important enough. So, sensitivity of the determination of alkali-earth metals in the presence of H_3PO_4 in acetylene-air oxidizing flame is ~ 2 times lower, than in stoichiometrical or reducing flame. In Table 2 optimum operating conditions for the determination a number of elements in phosphate solutions are resulted. It is found that the optimal fuel/oxidant ratio does not depend on the sample matrix. Fig. 4 demonstrates dependences of analytical signals of Mg, Ca, Sr, Ba, Al and Y from the height of the burner

for the solutions of different composition. It can be seen that there is a correlation between the maximum of analytical signal and the height of the inner cone. In the presence of a "heavy" matrix the specified maximums shift to a hotter flame zone which is located directly over an inner cone or close to it. In some cases (see curves *a*, *e*) maximums are diffuse. Buffer additions of chlorides of alkali metals have no effect on the position of maximum. Also, it is found that analytical signals of alkali metals do not depend considerably on the height of the burner.

Element	Method	Wavelength, nm	Flame ¹	Gas flow rate, L h ⁻¹		Height of inner cone, mm	Burner height, mm
				Combustible gas	Oxidant		
Li	FAES	670.8	AA (PBNO)	100 (85)	620 (600)	3	6...9
Na		589.0					
K		766.5					
Rb		780.0					
Cs		852.1					
Mg	FAAS	285.2	AA	95	620	2...3	8...9
			PBNO	60	600	2...3	7...8
			ANO	480	580	10	9
Ca	FAES	422.7	ANO	425	580	1...2	5...6
Sr	FAES	460.7	ANO	440	580	2	5...6
Ba	FAES	535.5	ANO	440...450	580	2...4	5...6
Al	FAES	396.1	ANO	490	560	5...10	9
	FAAS	309.2	ANO	530	560	15...20	8
Y	FAAS	410.2	ANO	550	560	25...30	12
Nd	FAES	492.4	ANO	515...530	580	30	10
Ti	FAAS	365.3	ANO	515...530	580	30...35	10
V	FAAS	318.4	ANO	515...530	580	30...35	10
Co	FAAS	240.7	ANO (PBNO)	70 (60)	690 (600)	1...2	6...9
Ni	FAAS	232.0	ANO (PBNO)	70 (60)	690 (600)	1...2	6...9

Table 2. Optimum operating conditions of the atomizer

Generally, change of optimum fuel/oxidant ratio as well as the height of the burner can lead to the considerable decrease in sensitivity and increase uncertainty in FAES and FAAS analyses of phosphate solutions.

¹ AA - acetylene-air, PBNO - propane-butane-nitrous oxide, ANO - acetylene-nitrous oxide

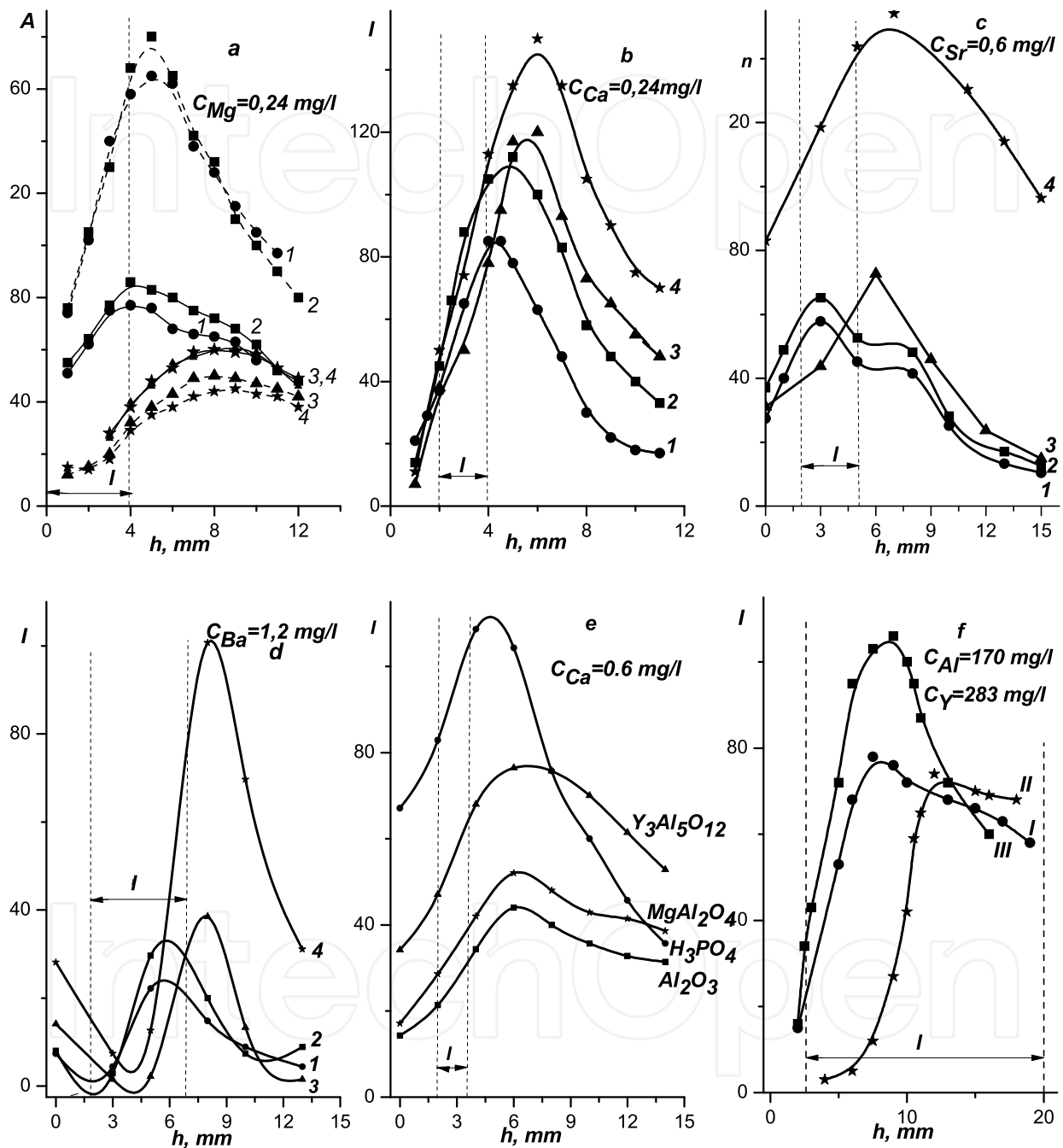


Fig. 4. Dependence of absorption signals (A) of Mg (a), Al^I and Y^{II} (f) and emission signals (I) of Ca (b, e), Sr (c), Ba (d), Al^{III} on the height of the burner (h, mm). Flames: acetylene-air (- · - · -), acetylene - nitrous oxide (---), propane - butane - nitrous oxide (- - -). 1 - model solution of element; 2 - Element + H₃PO₄; 3 - Element + H₃PO₄ + CdWO₄; 4 - Element + H₃PO₄ + CdWO₄ + NaCl. l - position of inner cone

2.2.2 Solvent effects on the absorption and emission spectra of analysed elements

Effect of phosphate ions on analytical signals of alkali, alkali-earth, transition and other elements was studied in detail in many papers (Magyar, 1987; Smets, 1980). However, these results look rather discordant. This fact can be explained by variety of spectrometers and hardware parameters used as well as by quite different concentrations of phosphate ions and analysed elements.

Therefore, effect of phosphate ions on emission signals of Al, alkali, alkali-earth elements and absorption signals of Mg, Al, Y, Ti, V, Fe, Co, Ni in different flames at the constant concentration of the phosphoric acid (12.4 mas. %) has been investigated. The results presented in Fig. 5 show that effect of a phosphoric acid on analytical signals is various.

In an acetylene-air flame H_3PO_4 shows strong depressing effect on all alkali elements. This effect increases in the order $Li < Na, K < Rb < Cs$, that is in a good agreement with the literary data (Henrion et al., 1979). In a propane-butane-nitrous oxide flame effect of H_3PO_4 on Li, K signals practically misses. For Rb and Cs the depressing effect is smaller, and for Na is greater, than in an acetylene-air flame.

It is noted that effect of phosphate ions on analytical signals of analysed elements depends essentially on a composition of gas mixture. For example, in an oxidative acetylene-air flames an emission signal of K in the presence of H_3PO_4 decreases for 90 %, whereas in a stoichiometrical flame it decreases for 70 %. It is noted also that a continuous background caused by presence of a phosphoric acid is much lower in a stoichiometrical flame, rather than in oxidative or reducing one. Apparently, character of effect of phosphate ions on analytical signals in various flames is caused not only their temperature, but composition also. It is possible to explain depressing activity of phosphates by formation of hardly vaporable compounds. Such effect is more typical for an acetylene-air flame.

It is found that phosphoric acid in an acetylene-air flame has small depressing effect on an absorption signal of Mg which is incremented with augmentation of the content of this element. In a propane-butane-nitrous oxide flame, effect of phosphates on an absorption signals of traces of Mg is absent, whereas at high concentrations of Mg its analytical signal slightly decreases. Emission signals of Ca, Sr, Ba, Nd and absorption signals of Ti and V in an acetylene-nitrous oxide flame in the presence of a phosphoric acid increase by 20, 22, 13 and 9 %, respectively. Apparently, it is possible to explain these phenomena by the fact that a high temperature of a flame and a reducing medium (red zone) promotes more effective atomisation of substance. Phosphoric acid can interfere with formation of carbides of the Ti and V in a reducing red zone and as it stated in (Magyar, 1987), promotes formation more volatile oxides of metals (for example, V_2O_5 is more flying oxide than other oxides of this element).

The phosphoric acid depresses absorption signals of Fe, Ni, Co (by 20-23 %) both in acetylene-air and propane-butane-nitrous oxide flames, irrespective of their redox characteristics. The received results differ from ones described in (L'vov et al., 1975) in which it is specified that effect of acids on Fe group elements in an oxidative acetylene-air flame misses.

Thus, effect of phosphate ions on analytical signals of analysed elements depends on the physicochemical characteristics of elements, their concentration in phosphate solution and operation parameters of an atomizer.

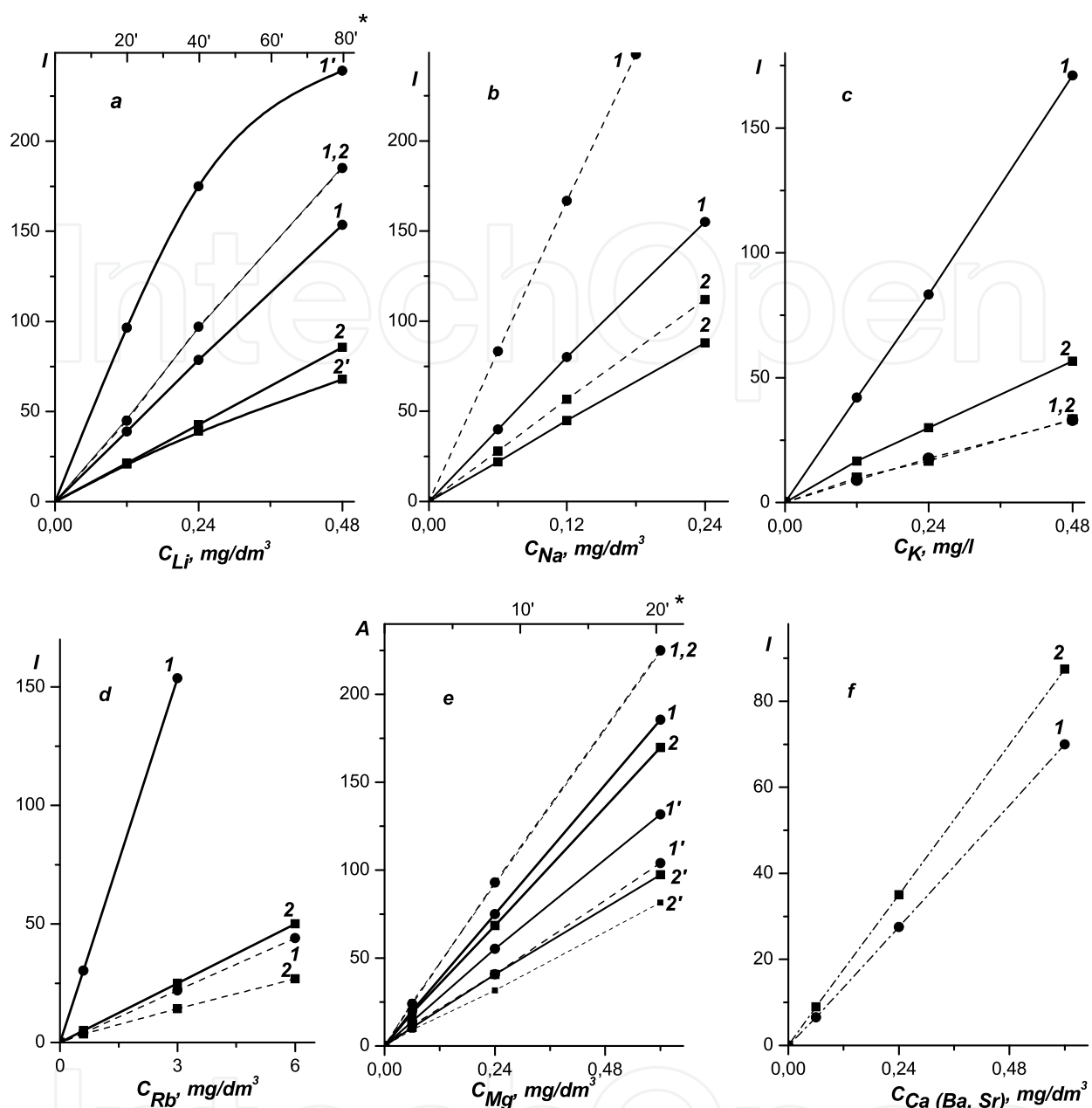


Fig. 5. Effect of H_3PO_4 on emission analytical signals (I) of alkali and alkali-earth elements (a, b, c, d, f) and absorption signals (A) of Mg (e) in acetylene-air (---), acetylene - nitrous oxide (- · - · -), propane-butane - nitrous oxide (- - -). Curves 1, (1') - model solution of element; 2, 2' - element + H_3PO_4 . *The burner is perpendicular to the optical axis

2.2.3 Matrix effects

Results of investigation of effect of major elements (Al, W, Ti) of high-melting compounds on analytical signals of analysed elements are presented in Table 3. Concentration of the phosphoric acid was 12.4 mas. %. Measurement conditions matched those given in Table 2. One can see that in comparison with effect of a phosphoric acid, Al increments emission signals of Li and Na. With increase of the Na concentration the rate of this effect decreases. Al shows depressing effect on the emission signal of K, and the rate of this effect depends on redox characteristics of a flame and is incremented with decrease of the content of a

combustible gas in a gas mixture. Increase in analytical signals of Na in the yttrium-aluminium garnet matrix is observed, whereas analytical signals of K do not change substantially.

Element	Concentration, ppm	Flame ²	Relative intensity of signals					
			H ₃ PO ₄	Al ₂ O ₃	Y ₃ Al ₅ O ₁₂	MgAl ₂ O ₄	CdWO ₄	SrTiO ₃
Li	0,2...6,0 %	AA	0.22					
	10...500	AA	0.55	1.08			0.98	
	10...500	PBNO	1.00				0.97	
Na	2,0...8,0 %	AA	0.86	1.08				
	0,2...1,0 %	AA	0.85	1.14				
	5...200	AA	0.52	1.14	1.12		1.00	
	5...200	PBNO	0.27				1.00	
K	10...500	AA	0.30	0.89	1.01		1.00	
	10...500	PBNO	1.00				1.00	
Rb	10...500	AA	0.17				0.98	
	10...500	PBNO	0.55				0.97	
Cs	10...500	AA	0.14				0.98	
	10...500	PBNO	0.53				1.08	
Mg	0,2...2,0 %	AA	0.74					
	0,2...2,0 %	PBNO	0.81					
	5...50	AA	0.90	0.30			0.55	
	5...50	PBNO	1.00	1.00			0.95	
Ca	5...200	ANO	1.25	0.39	0.78	0.45	1.10	1.55
Sr	10...100	ANO	1.28				1.10	
Ba	10...500	ANO	1.50				1.48	
Ti	200...2400	ANO	1.06	1.30				
V	200...2400	ANO	1.08	1.25		1.25		
Ni	200...2400	AA	0.79	0.50		0.50		
		PBNO	0.76	0.90		0.90		
Co	200...2400	AA	0.81	0.99		1.00		
		PBNO	0.80	1.13		1.12		
Nd	2,0...10,0 %	AA	1.08	2.04				

Table 3. Effect of matrix components on analytical signals of elements

An absorption signal of Mg in the presence of Al decreases slightly and with increase of the Mg concentration the rate of effect of Al increases. Use of a propane-butane-nitrous oxide flame allows analyst to eliminate matrix effect completely.

Aluminium based compounds (Al₂O₃, magnesium aluminium spinel, yttrium-aluminium garnet) show depressing effect on analytical signals of Ca, even in a high-temperature acetylene-nitrous oxide flame. The rate of depressing effect increases in the order yttrium-aluminium garnet < magnesium aluminium spinel < Al₂O₃ which is correlated with aluminium content in these compounds. Increase in analytical signals of Ca in SrTiO₃ matrix can be explained by the fact that Sr acts as an ionization buffer (Havezov,1983).

² AA - acetylene-air, PBNO - propane-butane-nitrous oxide, ANO - acetylene-nitrous oxide

Results of our investigations have shown that absorption signals of hardly volatile elements such as Ti and V, and emission signals of Nd in the presence of Al_2O_3 are increased. Probably, it can be explained by decrease of partial pressure of elemental oxygen and the considerable facilitation of atomisation of oxides of analysed elements in the presence of aluminium (Grossmann, 1987).

In an acetylene-air flame Al demonstrates depressing effect on analytical signals of nickel and cobalt which is more substantial for Ni. On the contrary, absorption signals of Co and Ni in a propane-butane-nitrous oxide flame are increased.

It is known from the literary (Henrion et al., 1979) that W has a depressing effect on emission signals of alkali metals which is incremented in the order $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$. As have shown results of our investigations, in the presence of cadmium and phosphate ions, tungsten acts quite differently. As can be seen from Table 3, a cadmium tungstate matrix does not affect analytical signals of alkali metals in acetylene-air and propane-butane-nitrous oxide flames.

Absorption signals of Mg in a cadmium tungstate matrix in acetylene-air and propane-butane-nitrous oxide flames are reduced by 80 and 30 %, respectively. This matrix has a weak depressing effect on emission signals of alkali-earth elements in an acetylene-nitrous oxide flame.

Thus, character and power of matrix effect in phosphoric acid solutions of examined materials depend on the nature of the element to be analysed, measurement conditions and a composition of a gas mixture. Optimisation of these parameters allows analyst to minimise matrix effect.

2.2.4 Interference effects of analysed elements in phosphate solutions

Avoiding of interference effects is of significant importance in the high-precision determination of a stoichiometric composition of functional materials. Study of interferences of Mg, Al and Y in yttrium-aluminium garnet and magnesium aluminium spinel was performed using solutions prepared by digestion in a phosphoric acid of oxides and mixtures of oxides of these elements. The content of each oxide in a mixture matched to stoichiometric relationships $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ and $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or by 2-5 times differed from them. The content of dissolved oxides in solutions was $0.5\text{-}3 \text{ g L}^{-1}$. It was found that in an acetylene-air flame a strong depressing effect of Al on absorption signals of Mg is observed. In a propane-butane-nitrous oxide flame this effect is weaker, whereas in an acetylene-nitrous oxide flame it is insignificant (Fig. 6). Authors (Havezov, 1983; Lueske, 1992) explained this fact by formation of MgAl_2O_4 spinel which stability depends on the composition of a flame and temperature. Magnesium reduces emission and absorption signals of Al that leads to parallel shift of the calibration line without change its bias. In the presence of Y the small increase of emission signals of Al is observed. At the same time Y does not affect absorption signals of Al. Analytical signals of Y decrease in the presence of Al (Fig. 6b).

For elimination of such interferences a lanthanum nitrate modifier is found to be the most effective. Introduction in solutions not less than 1 mas. % of the lanthanum interfering with forming low-volatile compounds at the moment of evaporation of droplets of an aerosol [], allows to eliminate all interferences almost completely (except depressing effect of Al on absorption signals of Mg in an acetylene-air flame). The content of $n \cdot \text{Y}_2\text{O}_3 \cdot k\text{Al}_2\text{O}_3$ or $\text{MgO} \cdot k\text{Al}_2\text{O}_3$ (at $k < 3$) in solutions should not exceed 1 g L^{-1} or 0.5 g L^{-1} of $\text{MgO} \cdot k\text{Al}_2\text{O}_3$ (at $k > 3$). In order to prevent precipitation of lanthanum compounds, analysed solutions should contain not less than 1.4 M of HNO_3 .

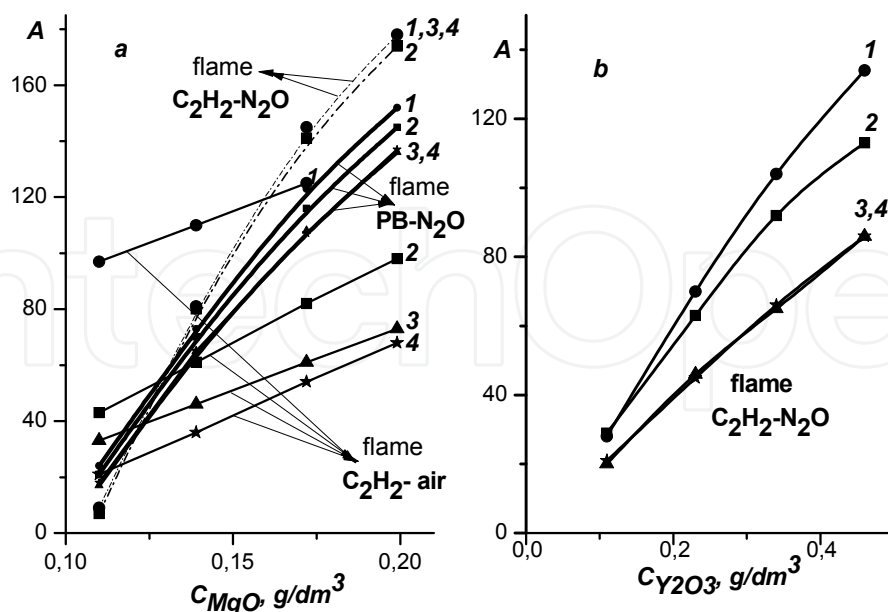


Fig. 6. Influence of Al on absorption signals of Mg (a) in acetylene-air, propane-butane-nitrous oxide and acetylene-nitrous oxide flames; Y (b) in an acetylene-nitrous oxide flame. 1 - Mg (Y) + H₃PO₄; 2 - Mg (Y) + H₃PO₄ + Al; 3 - Mg (Y) + H₃PO₄ + Al + La

It was also found that interferences of Na, K, Ca, Mg during their determination in CdWO₄, Al₂O₃, yttrium-aluminium garnet and magnesium aluminium spinel can be eliminated by using of a cesium chloride buffer. In this case, it is possible to determine all these elements from the same solution.

2.2.5 Some practical applications of phosphoric acid digestion of refractory oxide single crystals followed by flame spectrometry analysis

Our investigations have shown efficiency of use of a condensed phosphoric acid for dissolution of different refractory oxide single crystals. The data presented in the previous sections were used for the development of new procedures for determination of main components, dopants and microimpurities in single crystals and raw materials.

For the determination of a stoichiometric composition of yttrium-aluminium garnet and magnesium aluminium spinel, powder reference materials 3Y₂O₃·5Al₂O₃ and MgO·Al₂O₃ were used. The content of metals in these compounds was determined precisely by chelatometry. Calibration standards were prepared by dissolving of different masses of a powder reference material in condensed phosphoric acid. All solution contained CsCl as a spectroscopic buffer. An acetylene-nitrous oxide flame was used in the most cases but the determination of Mg is also possible with use of a propane-butane-nitrous oxide flame. Tables 4 and 5 contain data on the methods accuracy check and comparison with the results of chelatometry (in terms of oxides).

As can be seen from the Table 4, high concentrations of Al can be determined by both FAES and FAAS methods but the last one is more preferable. It was found that K and Na can be determined in sparingly soluble tungstates KGd(WO₄)₂ and BiNa(WO₄)₂ after their dissolving in a condensed phosphoric acid with a confidence interval not exceeding 0.5...0,7

mas. %. Moreover, the absence of matrix effect allowed carrying out the analysis with use of calibration standards containing solvent and analysed elements only (CsCl was used a spectroscopic buffer for the determination of Na).

Material	Oxide	Method	Abundance, mas. %		df ³	RSD%	<i>t</i> -test (critical value, P=0.95)
			Stated	Found			
Yttrium-aluminium garnet	Al ₂ O ₃	FAES	42.8	42.7	36	1.2	1.19 (2.02)
		FAAS	42.8	42.8	44	1.2	0 (2.02)
		FAES	31.4	31.2	24	2.1	1.67 (2.06)
		FAAS	31.4	31.5	40	2.2	0.98 (2.02)
	Y ₂ O ₃	FAAS	56.8	56.7	44	1.8	0.68 (2.02)
		FAAS	68.8	69.1	42	2.3	1.31 (2.02)
Magnesium aluminium spinel	Al ₂ O ₃	FAES	70.2	69.9	21	1.0	2.19 (2.08)
		FAAS	70.2	70.3	48	1.0	0.98 (2.01)
	MgO	FAAS	27.2	27.3	35	1.1	1.97 (2.03)
		FAAS (propane-butane-nitrous oxide flame)	27.2	27.2	33	0.8	0 (2.01)

Table 4. Accuracy check of the developed procedures

Compound	Oxide	Technical requirements, mas. %	Found, mas. %	
			FAAS	Chelatometry
3Y ₂ O ₃ · 5Al ₂ O ₃	Y ₂ O ₃	57.1 ± 1.3	56.4 ± 0.6	56.8 ± 0.2
	Al ₂ O ₃	42.9 ± 1.0	42.6 ± 0.3	42.7 ± 0.1
Y ₂ O ₃ · Al ₂ O ₃	Y ₂ O ₃	68.9 ± 1.0	69.2 ± 1.0	69.2 ± 1.0
	Al ₂ O ₃	31.1 ± 0.5	31.2 ± 0.4	31.2 ± 0.4
MgO · Al ₂ O ₃	MgO	27.2 ± 0.5	27.2 ± 0.1	27.2 ± 0.1
	Al ₂ O ₃	70.3 ± 1.3	70.3 ± 0.5	70.2 ± 0.2

Table 5. Comparison of results obtained by chelatometry and FAES (*n*=3; P=0.95)

Accuracy of developed procedures for the determination of dopants in aluminium oxide based materials was checked by comparison with results obtained by an independent method as well as using a different method of sample preparation (Table 6). The proposed procedures are more precise than arc atomic emission analysis and do not require large amounts of samples as is required in X-ray fluorescence analysis.

³ Number of degrees freedom

Compound	Element	Concentration, mas. %		
		Flame spectrometry		Arc atomic-emission spectroscopy
		Condensed phosphoric acid digestion	Fusion with LiBO ₂	
α -Al ₂ O ₃	Ti	(2.4±0.2) · 10 ⁻²	(2.5±0.1) · 10 ⁻²	(10±2) · 10 ⁻² (3.0±0.3) · 10 ⁻²
	V	(8.4±0.4) · 10 ⁻²		
	Ni	(2.5±0.2) · 10 ⁻²		
β -Al ₂ O ₃	Na	4.4±0.1	4.3±0.2	
		3.0±0.1	2.8±0.2	
		5.0±0.1	5.1±0.2	
		8.0±0.1	8.0±0.2	
Yttrium-aluminium garnet	Nd	0.77±0.04	0.76±0.02	0.85±0.06 1.40±0.09
		1.24±0.04	1.27±0.03	

Table 6. Results of the determination of dopants in aluminium oxide based materials ($n=3$; $P=0.95$)

Some metrological characteristics of developed procedures are presented in the Table 7. Thus, phosphoric acid digestion is a very effective and universal method of sample preparation of refractory oxide single crystals and raw materials. In some cases this is the only method suitable for the successive determination of alkali metals in single crystals since sample solutions obtained by alkali fusion may have extremely high blank signals.

Compound	Element	Concentration range, mac. %	RSD%	Typical abundance of the element, mas. %
α -Al ₂ O ₃ , m Al ₂ O ₃ · n MgO	Dopants			
	Ti	1·10 ⁻² ...2.0	14...4	5·10 ⁻³ ...0.4
	V	5·10 ⁻³ ...2.0	10...3	5·10 ⁻³ ...0.4
	Co (AA)	7·10 ⁻³ ...2.0	15...2	0.01...0.6
	Co (PBNO)	7·10 ⁻³ ...2.0	13...2	
	Ni (AA)	7·10 ⁻³ ...2.0	12...2	<7·10 ⁻³ ...0.13
	Ni (PBNO)	7·10 ⁻³ ...2.0	9...2	
β -Al ₂ O ₃	Li	1·10 ⁻³ ...10.0	5...1	1·10 ⁻³ ...0.7
	Na	0.2...10.0	4...2	0.7...6.0
	Mg (AA)	0.2...2.0	4...1	0.8
	Mg (PBNO)	0.2...2.0	1	
m Al ₂ O ₃ · n Y ₂ O ₃	Nd	0.2...6.0	11...5	0.5...4.2
α -Al ₂ O ₃	Impurities			
	Na	5·10 ⁻⁴ ...2·10 ⁻²	14...7	<5·10 ⁻⁴ ...0.19
	K	1·10 ⁻³ ...5·10 ⁻²	13...2	<1·10 ⁻³ ...0.06
	Ca	1·10 ⁻³ ...2·10 ⁻¹	10...2	1·10 ⁻³ ...0.03
m Al ₂ O ₃ · n Y ₂ O ₃	Na	5·10 ⁻⁴ ...2·10 ⁻²	12...3	<5·10 ⁻⁴ ...7·10 ⁻³
	K	1·10 ⁻³ ...5·10 ⁻²	13...2	<5·10 ⁻⁴ ...9·10 ⁻³
	Ca	5·10 ⁻⁴ ...2·10 ⁻²	13...9	7·10 ⁻⁴ ...2·10 ⁻³

Compound	Element	Concentration range, mac. %	RSD%	Typical abundance of the element, mas. %
CdWO ₄	Li	1·10 ⁻⁴ ...4·10 ⁻³	6...3	<1·10 ⁻⁴
	Na	1·10 ⁻⁴ ...2·10 ⁻³	7...3	2·10 ⁻⁴ ...1·10 ⁻²
	K	2·10 ⁻⁴ ...2·10 ⁻³	6...2	<2·10 ⁻⁴
	Rb	5·10 ⁻⁴ ...2·10 ⁻²	5...2	<5·10 ⁻⁴
	Cs	5·10 ⁻³ ...2·10 ⁻¹	6...2	<5·10 ⁻³
	Mg, Ca	1·10 ⁻⁴ ...1·10 ⁻²	6...2	<1·10 ⁻⁴
	Sr	3·10 ⁻⁴ ...1·10 ⁻²	2...1	<2·10 ⁻⁴
	Ba	1·10 ⁻² ...2·10 ⁻²	3	<5·10 ⁻³
SrTiO ₃	Ca	5·10 ⁻⁴ ...3·10 ⁻²	4...2	4·10 ⁻⁴

Table 7. Metrological characteristics of procedures of flame spectrometry analysis of single crystals with phosphoric acid digestion at the stage of sample preparation

3. Analysis of aqueous extracts of powders based on aluminium oxide

The traditional methods of sample preparation of aluminium oxide such as fusion with fluxes and selective acid dissolution in autoclaves are time consuming and unsafe.

Digestion of oxide materials in condensed phosphoric acid is express and reliable method. However, a strong depressing effect of phosphoric acid on analytical signals in atomic spectrometry does not allow to provide low detection limits for many elements. Recently, procedures of the direct analysis of oxide materials from aqueous suspension are widely used, but this method (see section 4) requires use of standards identical to analysed samples. This section contains results of the study of aqueous extraction of K, Na, Ca, V, Ni and Co from α -, γ -Al₂O₃, m Al₂O₃· n Y₂O₃ and m Al₂O₃· n MgO used as raw materials for single crystals growing.

3.1 Flame spectrometry determination of alkali metals and Ca in aqueous extracts of α - and γ -Al₂O₃

Commercially available extra pure γ -Al₂O₃ powders (Donetsk Plant for Chemical Reagents, Ukraine) were used throughout. α -Al₂O₃ was obtained by calcination of ammonia alum at 1200 °C during 3 hours (Chebotkevich, 1975), Y₃Al₅O₁₂ was synthesized from Al₂O₃ and Y₂O₃ by calcination at 1200 °C (Neiman et al., 1980). α -Al₂O₃ was powdered in a leucosapphire mortar and sifted through 40, 60, 100 and 160 microns sieves. Particle size of γ -Al₂O₃ and Y₃Al₅O₁₂ initially was less than 1 μ m.

Leaching procedure was carried out in quartz beakers (50 ml) at ambient temperature by mixing of powders with ultrapure water to obtain stable suspension followed by spontaneous sedimentation of a solid phase. Heating of the sample has appeared unacceptable owing to oxide adherence to beaker walls. It was also found that the spontaneous sedimentation of Al₂O₃ solid phase and Al(OH)₃ formed during leaching is an optimum technique of sample preparation. Centrifugation of suspension is found to be unsuitable because of formation of very stable suspension. Especially, this is typical for fine powders of γ -Al₂O₃ and Y₃Al₅O₁₂.

Effect of α -Al₂O₃ particle size on the recovery of Na, K and Ca is shown in Fig. 7. One can see that the full extraction of elements is observed up to particle size < 60 microns and for K

even to < 100 microns. The average time of the spontaneous sedimentation of these oxide materials depends on the dispersity of powders and is equal to 8 hours for α -Al₂O₃ and 10-12 hours for γ -Al₂O₃ and Y₃Al₅O₁₂.

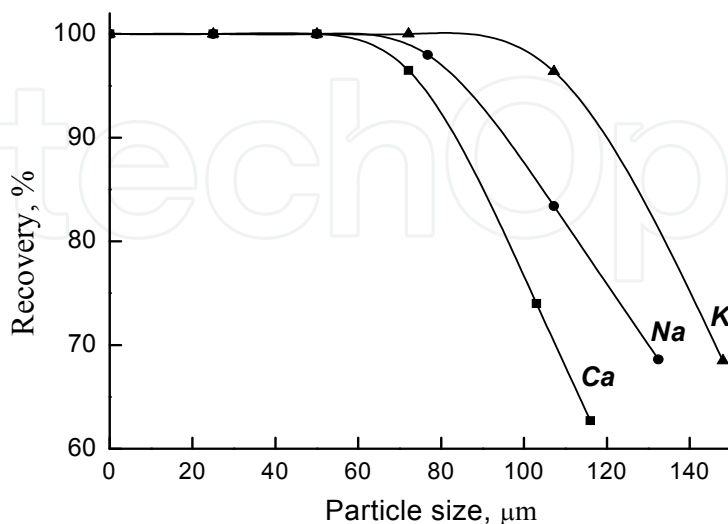


Fig. 7. Effect of α -Al₂O₃ particle size on the recovery of Na, K and Ca

It is possible to make the following assumptions concerning effects of transferring of impurities of alkali metals and Ca in an aqueous phase during the extraction procedure irrespective of Al₂O₃ modifications:

- along with increase of specific surface of materials during grinding, a great number of microinhomogeneities and defects are appeared on a surface of particles (Dobrovinskaya et al., 2007; Hanamirova, 1983; Foner, 1984);
- γ -Al₂O₃ and Y₃Al₅O₁₂ fine powders (<< 1 μm) are partly hydrated and some amounts of Al(OH)₃ are always present;
- after calcination of alum at temperature of 1200 °C there is a part of unevaporated sulphates of alkali metals in the obtained aluminium oxide. The full decomposition of sulphates takes place at higher temperatures (Chebotkevich, 1975; Hanamirova, 1983). Sulphates of alkali metals have a good solubility in water;
- it was experimentally confirmed by other authors (Ermolenko et al., 1971; Hanamirova, 1983; Uksche, 1977) that at temperatures of 600-1200 °C aluminate of alkali and alkali-earth element of spinel type are generated. Owing to a "quasiliquid" state of cationic sublattice ions of alkali metals can migrate freely via interblock clefts and substitute each other in the spinel cluster (Uksche, 1977). Aluminates of alkaline and alkali-earth metals in water are hydrolyzed to Al(OH)₃ and hydroxyaluminates (Hanamirova, 1983; Remi, 1973).

Apparently, in aqueous suspensions of Al₂O₃ and Y₃Al₅O₁₂ all these factors may take place and may have a different contribution depending on the dispersity and "prehistory" of material. It was found that the optimum sample mass/water volume ratio is 0.1 g per 10 ml of water. The time of obtaining of transparent extracts was 10 and 12 hours for α -Al₂O₃ and γ -Al₂O₃ (Y₃Al₅O₁₂), respectively. It is a compromise between the sensitivity of analysis and sample preparation time.

Optimum conditions of the flame spectrometry determination of Na, K and Ca in aqueous extracts of Al₂O₃ and Y₃Al₅O₁₂ have been studied. It has been found that Na, K and Ca

increase analytical signals of each other. Al and Y up to concentration of 10 mg L⁻¹ do not affect analytical signals of Na and Ca but increase the analytical signal of K. Using of CsCl as a spectroscopic buffer (2 g L⁻¹) has allowed us to eliminate interference effects completely.

The results of analysis of aluminium based oxide materials obtained using the proposed method of sample preparation and digestion in condensed phosphoric acid are shown in Table 8.

One can see that aqueous extraction technique provides lower limits of determination (LOD) of Na, K and Ca and does not yield to more complicated techniques described in (Krasil'shchik et al., 1989; Slovak et al., 1981). The developed technique can be used for the express quality control of fusion mixtures of Al₂O₃ and Y₃Al₅O₁₂ of different dispersity and for the determination of alkali metals dopants in Al₂O₃ charge.

Material	Element	Aqueous extracts			Digestion in condensed phosphoric acid		
		Found, ppm	RSD%	C _{min} , ppm	Found, ppm	RSD%	C _{min} , ppm
α- Al ₂ O ₃	Na	9,1±0,4	3	0.2	11±2	10	5
		67±2	2		66±5	6	
		28±1	2		28±2	4	
γ- Al ₂ O ₃		14±1	4		14±2	9	
α- Al ₂ O ₃	K	9,1±0,3	3	0.2	< 10	13	10
		43±2	1		40±4	7	
		130±3	2		140±8	4	
γ- Al ₂ O ₃		51±3	2		53±4	2	
α- Al ₂ O ₃	Ca	20±1	3	0.2	17±2	7	5
		29±1	3		28±2	4	

Table 8. Comparison of results obtained using two different methods of sample preparation ($n=3$; $P = 0.95$)

3.2 Flame spectrometry determination of dopants Co and Ni in subacid aqueous extracts of α- and γ-Al₂O₃

The possibility of application of subacid aqueous extraction technique combined with ultrasonic and microwave treatment for the determination of Co and Ni in α- and γ-Al₂O₃ fusion mixtures was studied.

An ultrasonic dispenser UZDN-A (Selmi, Ukraine) with operating frequency of 22 kHz a microwave digestion system MDS-2000 (CEM, USA) were used for the treatment of subacid aqueous suspensions of Al₂O₃ powders. Fractions with particle size less than 40 μm were used throughout. 0.1 g of α-Al₂O₃:Co(Ni) or mAl₂O₃ nMgO:Co(Ni) was mixed with 10 ml of water and 0.2 ml of HNO₃ and then ultrasonic treatment was applied. Solutions obtained after the spontaneous sedimentation of solid phase were used for analysis.

It was found that recovery of Co and Ni is quite similar and increases with augmentation of intensity of ultrasonic irradiation and processing time (Fig. 8 and 9). The maximum in Fig. 8 corresponds to optimum cavitation conditions. However, the maximum recovery at the optimum conditions ($I = 78$ W, $\tau = 15$ min) was only 50 %. It was assumed that only those atoms located on grains boundary (not entered into crystal lattice owing to various ionic radiuses of cobalt (nickel) and aluminium (Dobrovinskaya et al., 2007) have been extracted.

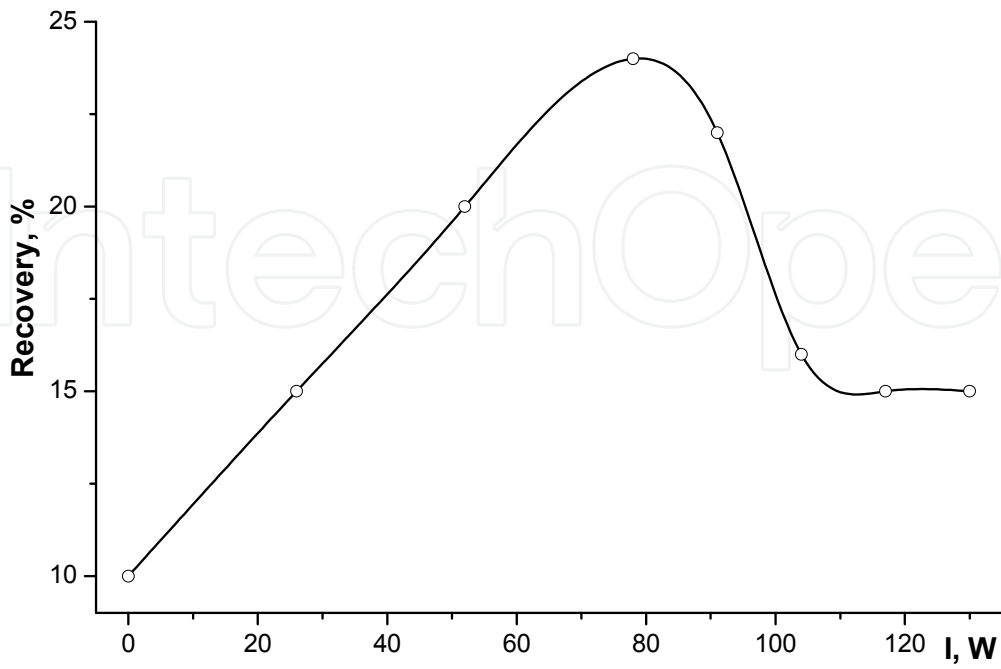


Fig. 8. Dependence of recovery of Co(Ni) on the ultrasonic dispenser driving power ($\tau = 5$ min)

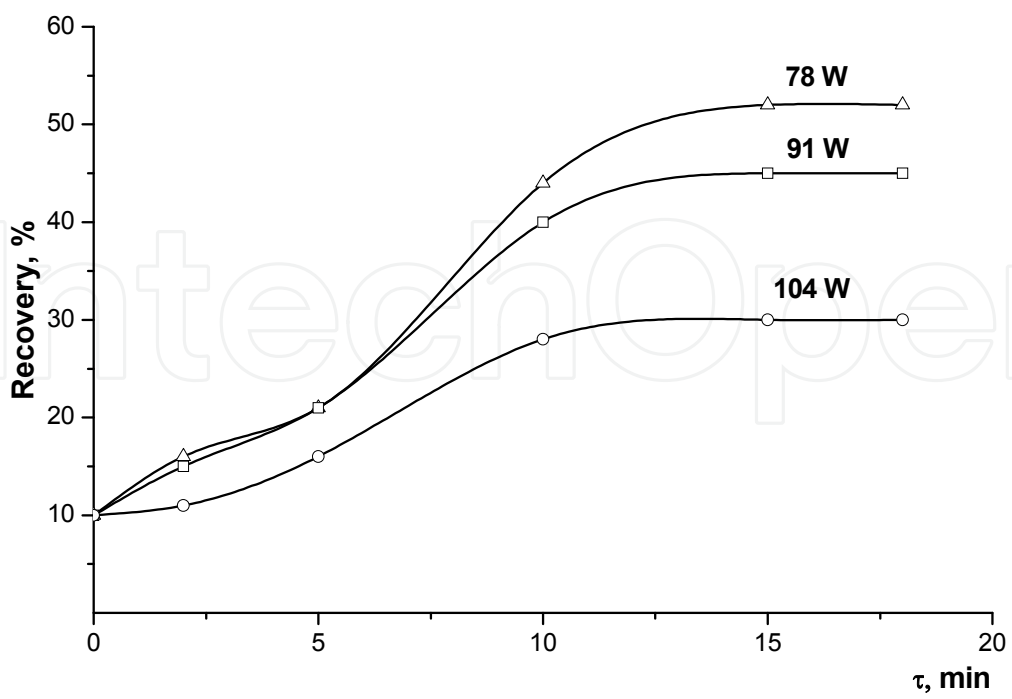


Fig. 9. Dependence of recovery of Co(Ni) on the exposure time

Thus, ultrasonic treatment of aqueous suspensions of Al_2O_3 powders is found to be unsuitable for quantitative analysis of extracts. However, as have shown our further investigations, it is possible to use successfully suspensions of $\alpha\text{-Al}_2\text{O}_3$ for direct determination of Co and Ni dopants (see section 4).

Extraction of Co and Ni from subacid aqueous suspensions of Al_2O_3 powders using microwave heating in closed vessels was found to be more effective. Dependence of recovery of Co and Ni on time of exposure (at pressure of 100 psi) and acidity of aqueous suspensions was studied. 0.05, 0.2, 0.5 and 1 ml of HNO_3 were added to 10 ml of aqueous suspensions of Al_2O_3 in order to obtain the samples with different acidity. As can be seen from Fig. 10, the most principal parameter is exposure time. Obviously, the transfer of dopants into solution under microwave heating is caused by deterioration of surface layers and activation of diffusion-controlled transfer processes.

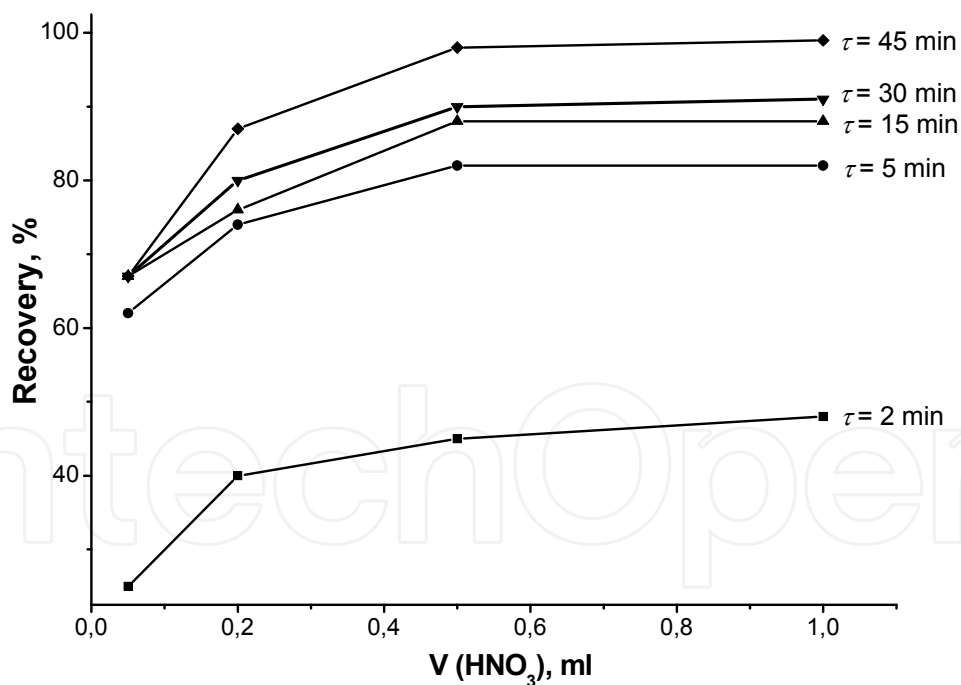


Fig. 10. Dependence of recovery of Co(Ni) on time of exposure and acidity of aqueous suspensions

Accuracy of the developed procedure for the determination of dopants in aluminium oxide based materials was proved by comparison with the results obtained by FAAS after digestion of samples in condensed phosphoric acid (Table 9). The obtained results are in good agreement with each other.

The proposed sample preparation technique has allowed us to improve limits of determination of Co and Ni owing to exclusion of acid solvents from analytical procedure and use of aqueous calibration standards.

Material	Element	Aqueous extracts			Digestion in condensed phosphoric acid		
		Found, ppm	RSD%	C_{min} , ppm	Found, ppm	RSD%	C_{min} , ppm
α - Al ₂ O ₃ : Co(Ni)	Ni	800 ± 20	2	10	810 ± 20	4	50
	Co	190 ± 10	4		210 ± 30	5	
m Al ₂ O ₃ · n MgO: Co(Ni)	Ni	1600 ± 20	1	10	1610 ± 20	5	50
	Co	790 ± 20	2		810 ± 20	4	

Table 9. Comparison of results of the determination of Co and Ni with use of two different sample preparation techniques ($n = 10$; $P = 0.95$)

4. Direct flame atomic absorption determination of Co and Ni dopants from aqueous suspensions of aluminium oxide based materials

Whereas Co and Ni dopants cannot be extracted quantitatively to aqueous phase during ultrasonic treatment of Al₂O₃ suspensions, it is possible to use directly such suspensions in analysis by flame atomic absorption spectrometry. Under ultrasonic irradiation the average size of suspended particles of a powder of Al₂O₃ decreases and suspension of very good stability and uniformity is formed. This is an important factor which affects degree of atomization and detection limits. For example, analytical signals of Co and Ni in such suspensions are two times higher in comparison with those obtained in suspensions prepared at ambient temperature by mechanical agitation. If there are certified reference materials available, this analysis technique has a number of benefits such as speed and low labor expenditures.

In this work calibration standards were prepared by using melt fusion technique. It was found that for the determination 100...2000 ppm of Co(Ni) it is necessary to have not less than five calibration standards with concentrations of an analyte increased by a factor of 2-2.5. Calibration standards were prepared as follows. Extra pure ammonia alum was melted in platinum crucible on a hot plate and then cobalt (or nickel) sulphate preliminary calcined

at 1200 °C was added. The melt was thoroughly stirred and dried under an infrared lamp. The solids was placed into a muffle furnace and heated slowly during 4 hours up to 1100 °C with subsequent holding during 3 hours with subsequent calcination at this temperature during 3 hours. After cooling aluminium oxide was ground to powder in a teflon mortal during an hour and sifted through a 40 µm sieve. Content of dopant in the prepared samples was approved by chelatometry. All subsequent procedures were the same as those described above.

Determined results were consistent with those obtained by analysis of samples digested in condensed phosphoric acid (Table 10).

As can be seen from Table 10, the proposed method has lower relative standard deviations as compared to the acid digestion procedure.

Element	Aqueous suspensions		Digestion in condensed phosphoric acid	
	Found, ppm	RSD%	Found, ppm	RSD%
Co	520 ± 20	4	510 ± 30	5
	990 ± 20	2	1100 ± 50	4
Ni	1100 ± 20	2	1100 ± 50	4
	2100 ± 40	2	2200 ± 70	3

Table 10. Comparison of results of the determination of Co and Ni with use of two different sample preparation techniques ($n = 6$; $P = 0.95$)

5. Conclusion

The results presented in this chapter show that flame atomic spectrometry can be successfully used for the express control of stoichiometric and impurity composition of refractory oxide single crystals such us Al_2O_3 , yttrium-aluminium garnet, cadmium tungstate, strontium titanate. Precision and accuracy of analytical procedure as well as metrological characteristics depend strongly on the technique of sample preparation. Use of condensed phosphoric acid as a solvent allows in comparison with traditional techniques of decomposition to unify a sample preparation procedure and to reduce the time of analysis by 5-10 times.

Optimum conditions of digestion of refractory oxide materials in condensed phosphoric acid are established. Influence of solvent, matrix and chemical interference effects on analytical signals of analysed elements with use of different mixed gas flames are also studied. It is shown that in some cases use of a propane-butane-nitrous oxide flame which is preferable and can significantly depress effects of macrocomponents and solvent. Determination of stoichiometric composition of single crystals requires paying much more attention to interference effects as well as matching of analysed materials to calibration standards as compared to impurities determination procedures.

The developed analytical procedures allow to evaluate major elements content such us Mg, Al and Y in different oxide compounds with relative standard deviations (%) 0.8...1.2, 1.0...1.5 and 1.5...2.5, respectively.

The proposed sample preparation methods for water extracts of aluminium oxide powders and yttrium-aluminium garnet allows to carry out an express determination of alkaline metals, calcium, nickel and cobalt in raw materials for single crystals growing. These sample preparation methods ensure low blank signals and better reproducibility of analytical signals as compared to acid digestion technique.

Limits of determination of impurities in all investigated materials after phosphoric acid digestion were 1...5 ppm. Na, K and Ca can be determined in aqueous extracts of Al_2O_3 with the limit of determination of 0.2 ppm.

It was shown that Co and Ni dopants can be determined by FAAS directly from aqueous suspensions of aluminium oxide based materials.

6. References

- Bock R. (1979). *A handbook of decomposition methods in analytical chemistry*. Glasgow, International Textbook Co. ISBN 0700202692 [Russian]
- Chebotkevich G.V. (1975). Calcination of aluminum ammonium alum. *Zhurnal prikladnoy khimii*, Vol. 48, No.2, pp. 414-417, ISSN 0044-4618 [Russian]
- Corbridge D.E.C. (1990). *Phosphorus: an outline of its chemistry biochemistry and technology*. 4-th edition. Amsterdam. Elsevier, ISBN 044-487-4380
- Dobrovinskaya E.; Lytvynov L.; Pischik V. (2007). *Sapphire in science and engineering*. Kharkov. STS «Institute for Single Crystals» National Academy of Sciences of Ukraine. ISBN 978-966-02-4589-1 [Russian]
- Ermolenko N.F.; Efros M.D.; Oboturov A.V. (1971). *Regulirovanie poristoi struktury okisnykh adsorbentov i katalisatorov*. Minsk. Nauka i tekhnologia. [Russian]
- Foner H.A. (1984). High-pressure acid dissolution of refractory alumina for trace element determination, *Analyt. Chem*, Vol. 56, No. 4, pp. 856-859, ISSN 0003-2700
- Grossmann O. (1987). Application of experimental design for investigating the determination of titanium in glass ceramics by flame atomic absorption spectrometry, *Anal. chim. acta*. V.203, No 1, pp. 55-66, ISSN 0003-2670
- Haines J.(1988). Sample preparation for AA, *Lab Pract*, Vol. 37, No. 10 pp. 85-86, 88, ISSN 0023-6853
- Hanamirova A. A. (1983). *Akumina and methods of reduction of the maintenance to it of impurity*. Er.: AN Arm. SSR [Russian]
- Hannaker P.; Qing-Lie H. (1984). Dissolution of geological material with orthophosphoric acid for major-element determination by flame atomic absorption spectroscopy and inductively-coupled plasma atomic-emission spectroscopy, *Talanta*, Vol. 31, No. 12, pp. 1153-1157, ISSN 0039-9140
- Haswell S.J.(1991). *Atomic absorption spectrometry*. Amsterdam. Elsevier, ISBN 0444882170
- Havezov I.P.; Tsalev D.L. (1983). *Atomic absorption analysis*. Leningrad, Khimia, [Russian]
- Henrion G.; Marquardt D.; Lunk H.-J. et al. (1979). Flammenphotometrische bestimmung von kaliumspuren in wolfram, *Z. Chem.*, Vol. 19, No. 10, pp 383-384, ISSN 0044-2402.

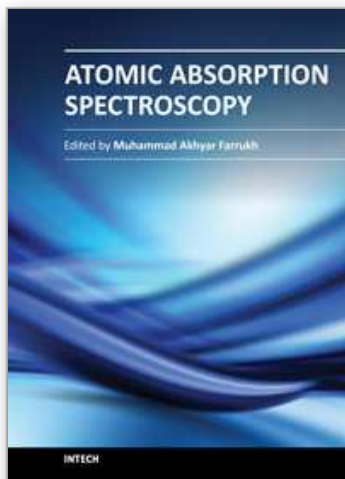
- Hill S.J. (2005). Atomic absorption spectrometry/ Flame. In: *Encyclopedia of Analytical Science (Second edition)*; Townshend A. (Ed.), Elsevier Ltd. pp. 163-170, ISBN 978-0-12-369397-6
- Homeier E.H.; Kot R.J.; Bauer L.J. et al. (1988). Dissolution of alfa alumina for elemental analysis by ICP-AES, *ICP Inf. Newslett.*, Vol. 13, No. 11, p. 716, ISSN 0161-6951
- Krasil'shchik V.Z.; Sukhanovskaya A.I.; Voronina G.A. et al. (1989). Atomic-emission and chemical atomic- emission analysis of aluminium compounds using inductive high-frequency discharge, *Zhurnal analiticheskoi khimii*, Vol. 44, No. 10, pp. 1878-1884, ISSN 0044-4502 [Russian]
- Krasil'shchik V.Z.; Zhiteleva O.G.; Sokol'skaya N.N. et al. (1986). Autoclave vapour-phase decomposition of some difficultly soluble substances, *Zhurnal analiticheskoi khimii*, Vol. 41, No. 4, pp. 586-590, ISSN 0044-4502 [Russian]
- Luecke W. (1992). Systematic investigation of aluminium interferences with the alkaline earths in flame atomic absorption spectrometry. 2. The behavior of magnesium and calcium, *Fr. Z. anal. Chem.*, Vol. 344, No. 6, pp. 242-246, ISSN 0937-0633
- L'vov B.V.; Kruglikova L.P.; Polzic L.K. et al. (1975). Theory of flame atomic absorption analysis. Communication 4. Calculated temperature values and equilibrium composition of acetylene- nitrous oxide and acetylene-air flames, *Zhurnal analiticheskoi khimii*, Vol. 30, No.5, pp. 846-852, ISSN 0044-4502 [Russian]
- L'vov B.V. & Orlov N.A. (1975). Theory of flame atomic absorption analysis. Communication . Effect of redox characteristics of flames and chemical form of atomized compounds on the degree of aerosol vaporization, *Zhurnal analiticheskoi khimii*, Vol. 30, No.9, pp. 1661-1667, ISSN 0044-4502 [Russian]
- Magyar B. (1987). Fundamental aspects of atomic absorption spectrometry, *CRC Crit. Rev. Analyt. Chem.*, Vol. 17, No. 2, pp. 145-191, ISSN 0007-8980
- Maitra A.M. (1987). Organophosphorus acid interferences in flame atomic absorption spectrometry, *Anal. chim. acta*, Vol. 193, No. 2, pp. 179-191, ISSN 0003-2670
- Mayer C.S., Tinoco C.M., Arraes I.P. (1985). Determination of chromium in geochemical sample by atomic absorption spectrometry, *Atom. Spectroscopy*, Vol. 6, No. 4, pp.121-122, ISSN 0195-5373
- Mirenskaya I.I., Shevtsov N.I., Blank A.B. et al. (1994). X-ray spectral determination of the stoichiometry of metal tungstate single crystals, *Zhurnal analiticheskoi khimii*, Vol. 49, No. 5, pp. 522-524, ISSN 0044-4502 [Russian]
- Mizoguchi T.; Ishii H. (1978). Analytical application of condensed phosphoric acid - I. determination of ferrous and total iron ores after decomposition with condensed phosphoric acid. 1978, *Talanta*. Vol. 25, No 6, pp. 311-316, ISSN 0039-9140
- Morikava H.; Ishizuka T. (1987). Determination of impurities in barium titanate by inductively coupled plasma atomic emission spectrometry, *Analyst*, Vol. 112, No. 7, pp. 999-1002, ISSN 0003-2654
- Nagornaya L.; Onyshchenko G.; Pirogov E. et al. (2005). Production of the high-quality CdWO₄ single crystals for application in CT and radiometric monitoring, *Nuclear*

- Instruments and Methods in Physics Research, Section A*, Vol. 537, No. 1-2, pp.163-167, ISSN 0168-9002
- Neiman A.Ya.; Tkachenko E.V.; Kvichko L.A. et al. (1980). Conditions and macromechanisms of the solid-phase synthesis of yttrium aluminates, *Zhurnal neorganicheskoi khimii*, Vol. 25, No.9, pp. 1294-1297, ISSN 0044-457X [Russian]
- Otruba V.; Navrátil D. (1990). Stanovení hliníku emisní plamenovou spektrometrií, *Chem. Listy*, Vol. 84, No. 8, pp. 862- . ISSN 1213-7103
- Patnaik P.; Dean J.A. (2004). *Dean's analytical chemistry handbook*. 2nd ed. Mc GRAW-Hill New York. ISBN 0-07-141060-0
- Pupyshev A.A.; Moskalenko N.I.; Muzgin V.N. et al. (1990). Atomisation of elements I acetylene-nitrous oxide flame, *Zhurnal analiticheskoi khimii*, Vol. 45, No. 12, pp. 2389-2399, ISSN 0044-4502 [Russian]
- Remi H. (1973). *Lehrbuch Der Anorganischen Chemie . I und II.*, Akadem Verlagsgesellschaft, Geest Portig.,Leipzig
- Rice T. D. (1977). Comparison of dissolution methods for the determination of potassium in rocks and minerals by atomic absorption spectrometry, *Anal. chim. acta*, Vol. 91, No. 2, pp. 221-228, ISSN 0003-2670
- Slovak Z., Docekal B. (1981). Determination of trace metals in aluminium oxide by electrothermal atomic absorption spectrometry with direct injection of aqueous suspensions, *Anal. chim. acta*. V.129, No 1, pp. 263-267, ISSN 0003-2670
- Smets B. (1980). Vaporisation interference of sulphate and phosphate anions on the calcium flame atomic absorption signal, *Analyst*, Vol. 105, No. 5, pp. 482-490, ISSN 0003-2654
- Stratis J.A.; Zachariadis G.A.; Dimitrakoudi E.A. et al. (1988). Critical comparison of decomposition procedures for atomic absorption spectrometric analysis of prehistorical ceramics, *Fr. Z. anal. Chem.*, Vol. 331, No. 7, pp. 725-729, ISSN 0937-0633
- Trachevskii V.V; Druzenko T.V; Potapova V.G. et al. (1996). Acidic-alkaline transformation of orthophosphoric acid on heating, *Ukrainskii khimicheskii zhurnal*, Vol. 62, No. 6, Pu pp. 84-88, ISSN 0041-6045 [Russian]
- Trachevskii V.V; Druzenko T.V; Potapova V.G. et al. (1996). NMR studying of metal oxide dissolution in phosphoric acids, *Ukrainskii khimicheskii zhurnal*, Vol. 62, No. 6, pp. 84-88, ISSN 0041-6045 [Russian].
- Tupitsyna I.A., Grinyov B.V.; KatrunovK.A. et al. (2009). Radiation Damage in CWO Scintillation Crystals With Different Defects, *IEEE Transactions on nuclear science*, Vol. 56, No. 5, pp. 2983-2988, ISSN 0018-9499
- Uksche E.A. (1977). Solid electrolytes, Moscow, Nauka [Russian]
- Welz B.; Sperling (1999). *Atomic Absorption Spectrometry*. Wiley-VCH, Weinheim, Germany. ISBN 3-527-28571-7
- Zolotovitskaya E.S.; Druzenko T.V. & Potapova V.G. (1997). Dissolution of refractory oxide materials in condensed phosphoric acid, *Zhurnal analiticheskoi khimii*, Vol. 52, No. 9, pp. 923-927, ISSN 0044-4502 [Russian]

Zolotovitskaya E.S.; Potapova V.G. (1984). Application of the phosphoric acid as solvent in the analysis of monocrystals based on aluminium oxide, *Zhurnal analiticheskoi khimii*, Vol. 39, No. 10, pp. 1781-1785, ISSN 0044-4502 [Russian]

IntechOpen

IntechOpen



Atomic Absorption Spectroscopy

Edited by Dr. Muhammad Akhyar Farrukh

ISBN 978-953-307-817-5

Hard cover, 258 pages

Publisher InTech

Published online 20, January, 2012

Published in print edition January, 2012

Atomic Absorption Spectroscopy is an analytical technique used for the qualitative and quantitative determination of the elements present in different samples like food, nanomaterials, biomaterials, forensics, and industrial wastes. The main aim of this book is to cover all major topics which are required to equip scholars with the recent advancement in this field. The book is divided into 12 chapters with an emphasis on specific topics. The first two chapters introduce the reader to the subject, its history, basic principles, instrumentation and sample preparation. Chapter 3 deals with the elemental profiling, functions, biochemistry and potential toxicity of metals, along with comparative techniques. Chapter 4 discusses the importance of sample preparation techniques with the focus on microextraction techniques. Keeping in view the importance of nanomaterials and refractory materials, chapters 5 and 6 highlight the ways to characterize these materials by using AAS. The interference effects between elements are explained in chapter 7. The characterizations of metals in food and biological samples have been given in chapters 8-11. Chapter 12 examines carbon capture and mineral storage with the analysis of metal contents.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

T.V. Sheina and K.N. Belikov (2012). Flame Spectrometry in Analysis of Refractory Oxide Single Crystals, Atomic Absorption Spectroscopy, Dr. Muhammad Akhyar Farrukh (Ed.), ISBN: 978-953-307-817-5, InTech, Available from: <http://www.intechopen.com/books/atomic-absorption-spectroscopy/flame-spectrometry-in-analysis-of-refractory-oxide-single-crystals>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen