6

Flame Spectrometry in Analysis of Refractory Oxide Single Crystals

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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 *a*- 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 a-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:

$$n\ H_3PO_4 \leftrightarrow H_{n+2}P_nO_{3n+1} + (n\text{-}1)\ H_2O$$

where n = 1…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:

$$PO_4^{3-} + n\ H^+ \leftrightarrow H_{3-n}PO_4, \qquad n = 0\ldots3$$

$$P_2O_4^{4-} + n\ H^+ \leftrightarrow H_{4-n}P_2O_7, \qquad n = 0\ldots4$$

$$P_3O_{10}^{5-} + n\ H^+ \leftrightarrow H_{5-n}P_2O_7, \qquad n = 0\ldots5$$

With driving off the water, the equilibrium $H_3PO_4 + H_2O \leftrightarrow H_3O^+ + H_2PO_4^-$ 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:

$$H_3PO_4 + H_4P_2O_7 \leftrightarrow H_4PO_4^+ + H_3P_2O_7^-$$

$$H_3PO_4 + H_5P_3O_{10} \leftrightarrow H_4PO_4^+ + H_4P_3O_{10}^-$$

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: $O^{2-} < OH^- < H_2O < H_3O^+$, (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}, °C); (c) average dissolution rate at fixed temperature (V, g min^{-1}); (d) degree of dissolution (*a*, %). Kinetics of dissolving *a*-Al_2O_3 and $CdWO_4$ was investigated. A mixture of 0.3 g of *a*-Al_2O_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.

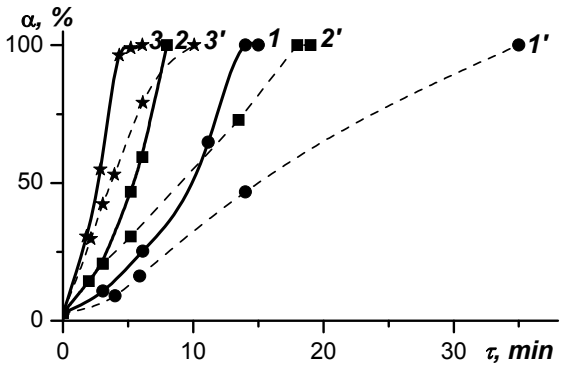

Fig. 1. Kinetics of dissolving Al_2O_3 (1′ - 3′) and $CdWO_4$ (1 -3) in condensed phosphoric acid: 215 °C (1, 1′), 270 °C (2, 2′), 330 °C (3, 3′).

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).

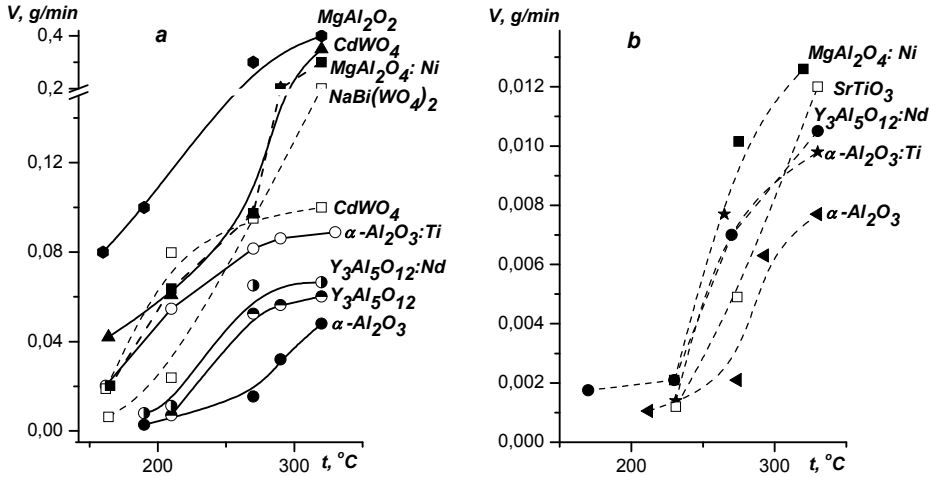

Fig. 2. Dependence of dissolution rate of different fusion mixtures (—) and single crystals (- - -) on temperature

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_2O_3 charge	0.3…0.4	270	16	0.05
α-Al_2O_3 single crystal	0.15	290…300	30	0.016
α-Al_2O_3:Ti charge	0.3	270	13	0.09
α-Al_2O_3:Ti single crystal	0.2	300	25	0.02
$m$$Al_2O_3$ ·$n$$Y_2O_3$ charge	0.3…0.4	270	11	0.07
$m$$Al_2O_3$ ·$n$$Y_2O_3$ ·$k$$Nd_2O_3$ charge	0.3…0.5	270	10	0.09
$m$$Al_2O_3$ ·$n$$Y_2O_3$ ·$k$$Nd_2O_3$ single crystal	0.2…0.3	300…320	20	0.05
$m$$Al_2O_3$ ·$n$$Mg$O charge	0.3…0.6	270	5	0.20
$m$$Al_2O_3$ ·$n$$Mg$O:Ni charge	0.3	270	6	0.20
$m$$Al_2O_3$ ·$n$$Mg$O: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-Al_2O_3; Ca in $SrTiO_3$; Na, K, Ca, Mg in $CdWO_4$; dopants Li, Na, Mg in β-Al_2O_3; Nd in yttrium aluminium garnet; Ti, V, Fe, Co, Ni in corundum; Li, Rb, Cs, Sr, Ba in $CdWO_4$; a stoichiometric composition of garnets $(n\text{-}x)Y_2O_3 \cdot xNd_2O_3 \cdot mAl_2O_3$ and $MgO \cdot kAl_2O_3$ 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.

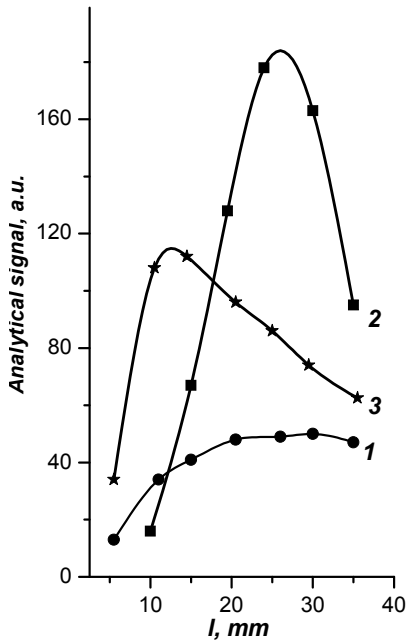

Fig. 3. Dependence of absorption signals of Al (1) and Y (2) and an emission signal of Al (3) in phosphate solutions of $Y_3Al_5O_{12}$ on the inner cone of the flame (*l*, mm*)*

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

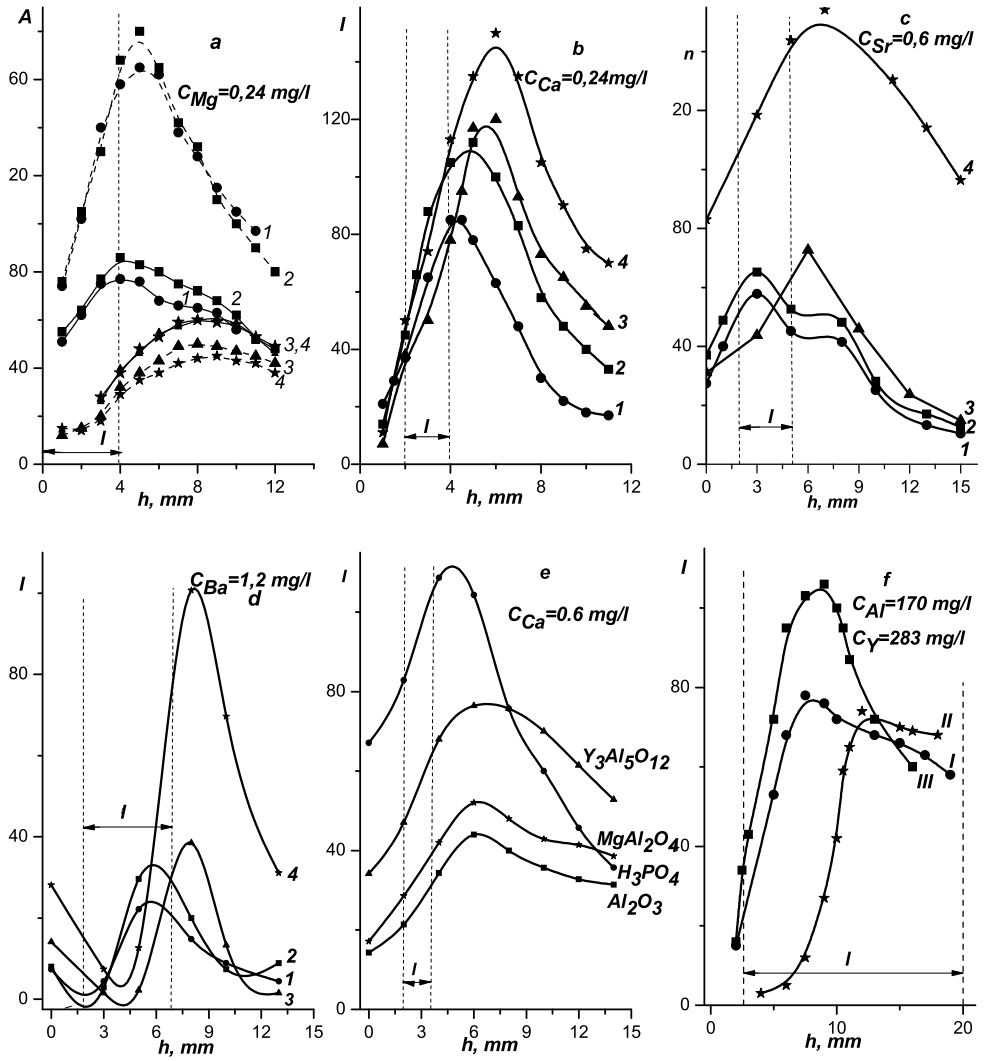

Fig. 4. Dependence of absorption signals (A) of Mg (a), Al^{I} and Y^{II} (f) and emission signals (I) of Ca (b, e), Sr (c), Ba (d), Al^{III} on the height of the burner (h, mm). Flames: acetylene-air (-·- ·-), acetylene – nitrous oxide (---), propane – butane - nitrous oxide (- - -). 1 – model solution of element; 2 – Element + H_3PO_4; 3 - Element + H_3PO_4 + $CdWO_4$; 4 - Element + H_3PO_4 + $CdWO_4$ + 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.

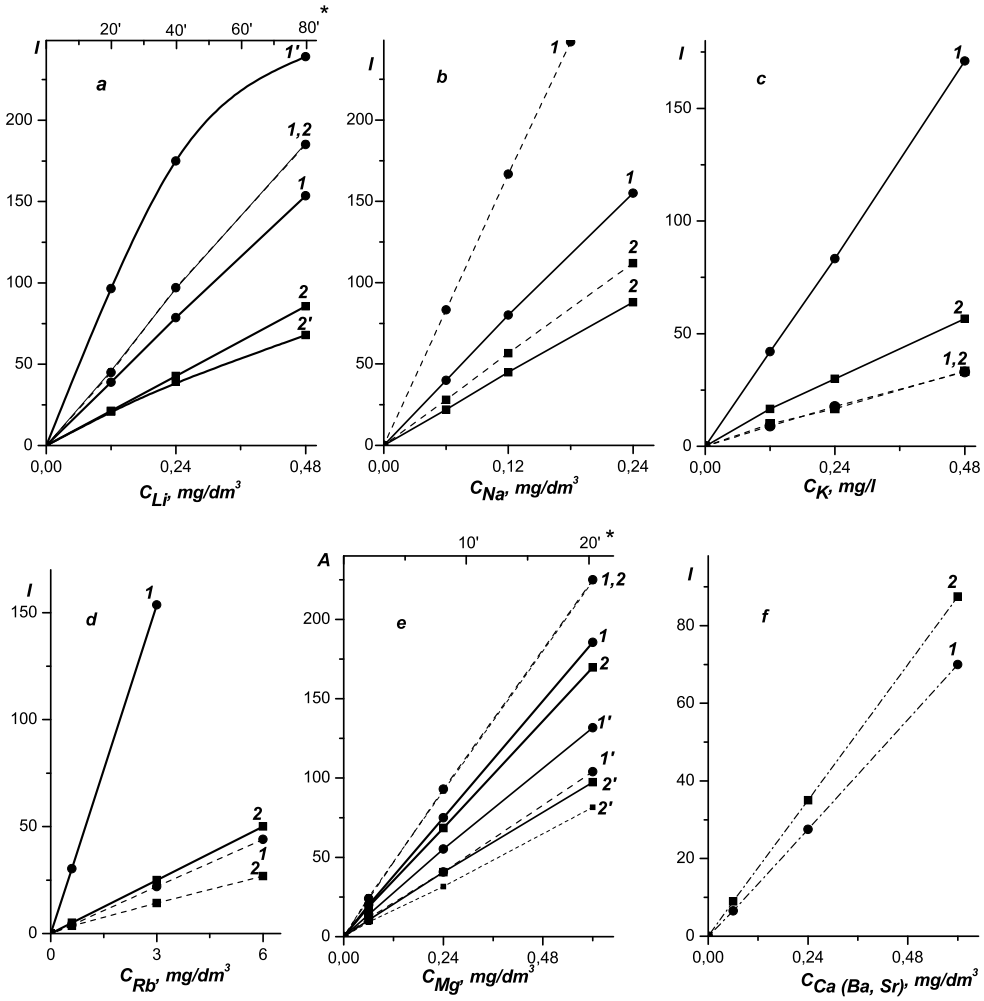

Fig. 5. Effect of H_3PO_4 on emission analytical signals (*I*) of alkali and alkali-earth elements (*a, b, c, d, f)* and absorption signals (A) of Mg (*e*) in acetylene-air (---), acetylene – nitrous oxide (- · - · -), propane- butane – nitrous oxide (- - -). Curves 1, (1′) – model solution of element; 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_3PO_4	Al_2O_3	$Y_3Al_5O_{12}$	$MgAl_2O_4$	$CdWO_4$	$SrTiO_3$
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 (Al_2O_3, 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 < Al_2O_3 which is correlated with aluminium content in these compounds. Increase in analytical signals of Ca in $SrTiO_3$ 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 Li < Na < K < Rb < 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 $3Y_2O_3 \cdot 5Al_2O_3$ and $MgO \cdot Al_2O_3$ or by 2-5 times differed from them. The content of dissolved oxides in solutions was 0.5-3 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 $n \cdot Y_2O_3 \cdot kAl_2O_3$ or $MgO \cdot kAl_2O_3$ (at k <3) in solutions should not exceed 1 g L^{-1} or 0.5 g L^{-1} of $MgO \cdot kAl_2O_3$ (at k >3). In order to prevent precipitation of lanthanum compounds, analysed solutions should contain not less than 1.4 M of HNO_3.

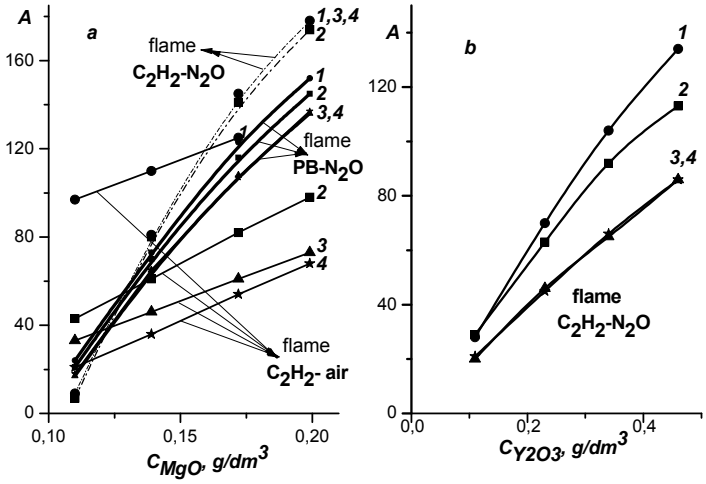

Fig. 6. Influence of Al on absorption signals of Mg (*a*) in acetylene-air, propane-butane-nitrous oxide and acetylene-nitrous oxide flames; Y (*b*) in an acetylene-nitrous oxide flame. 1 – Mg (Y) + H_3PO_4; 2 - Mg (Y) + H_3PO_4 + Al; 3 - Mg (Y) + H_3PO_4 + Al + La

It was also found that interferences of Na, K, Ca, Mg during their determination in $CdWO_4$, Al_2O_3, 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 $3Y_2O_3 \cdot 5Al_2O_3$ and $MgO \cdot Al_2O_3$ 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 $KGd(WO_4)_2$ and $BiNa(WO_4)_2$ 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%	*t*-test (critical value, P=0.95)
			Stated	Found			
Yttrium-aluminium garnet	Al_2O_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_2O_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_2O_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
$3Y_2O_3 \cdot 5Al_2O_3$	Y_2O_3 Al_2O_3	57.1 ± 1.3 42.9 ± 1.0	56.4 ± 0.6 42.6 ± 0.3	56.8 ± 0.2 42.7 ± 0.1
$Y_2O_3 \cdot Al_2O_3$	Y_2O_3 Al_2O_3	68.9 ±1.0 31.1 ± 0.5	69.2 ± 1.0 31.2 ± 0.4	69.2 ± 1.0 31.2 ± 0.4
$MgO \cdot Al_2O_3$	MgO Al_2O_3	27.2 ± 0.5 70.3 ± 1.3	27.2 ± 0.1 70.3 ± 0.5	27.2 ± 0.1 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_2O_3	Ti	$(2.4\pm0.2)\cdot10^{-2}$	$(2.5\pm0.1)\cdot10^{-2}$	
	V	$(8.4\pm0.4)\cdot10^{-2}$		$(10\pm2)\cdot10^{-2}$
	Ni	$(2.5\pm0.2)\cdot10^{-2}$		$(3.0\pm0.3)\cdot10^{-2}$
β-Al_2O_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
		1.24±0.04	1.27±0.03	1.40±0.09

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, мас.%	RSD%	Typical abundance of the element, mas. %
α-Al_2O_3, $mAl_2O_3\cdot nMgO$	Dopants			
	Ti	$1\cdot10^{-2}\ldots2.0$	14…4	$5\cdot10^{-3}\ldots0.4$
	V	$5\cdot10^{-3}\ldots2.0$	10…3	$5\cdot10^{-3}\ldots0.4$
	Co (AA)	$7\cdot10^{-3}\ldots2.0$	15…2	0.01…0.6
	Co (PBNO)	$7\cdot10^{-3}\ldots2.0$	13…2	
	Ni (AA)	$7\cdot10^{-3}\ldots2.0$	12…2	$<7\cdot10^{-3}\ldots0.13$
	Ni (PBNO)	$7\cdot10^{-3}\ldots2.0$	9…2	
β-Al_2O_3	Li	$1\cdot10^{-3}\ldots10.0$	5…1	$1\cdot10^{-3}\ldots0.7$
	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	
$mAl_2O_3\cdot nY_2O_3$	Nd	0.2…6.0	11…5	0.5…4.2
α-Al_2O_3	Impurities			
	Na	$5\cdot10^{-4}\ldots2\cdot10^{-2}$	14…7	$<5\cdot10^{-4}\ldots0.19$
	K	$1\cdot10^{-3}\ldots5\cdot10^{-2}$	13…2	$<1\cdot10^{-3}\ldots0.06$
	Ca	$1\cdot10^{-3}\ldots2\cdot10^{-1}$	10…2	$1\cdot10^{-3}\ldots0.03$
$mAl_2O_3\cdot nY_2O_3$	Na	$5\cdot10^{-4}\ldots2\cdot10^{-2}$	12…3	$<5\cdot10^{-4}\ldots7\cdot10^{-3}$
	K	$1\cdot10^{-3}\ldots5\cdot10^{-2}$	13…2	$<5\cdot10^{-4}\ldots9\cdot10^{-3}$
	Ca	$5\cdot10^{-4}\ldots2\cdot10^{-2}$	13…9	$7\cdot10^{-4}\ldots2\cdot10^{-3}$

Compound	Element	Concentration range, мас.%	RSD%	Typical abundance of the element, mas. %
$CdWO_4$	Li	$1\cdot10^{-4}\ldots4\cdot10^{-3}$	6…3	$<1\cdot10^{-4}$
	Na	$1\cdot10^{-4}\ldots2\cdot10^{-3}$	7…3	$2\cdot10^{-4}\ldots1\cdot10^{-2}$
	K	$2\cdot10^{-4}\ldots2\cdot10^{-3}$	6…2	$<2\cdot10^{-4}$
	Rb	$5\cdot10^{-4}\ldots2\cdot10^{-2}$	5…2	$<5\cdot10^{-4}$
	Cs	$5\cdot10^{-3}\ldots2\cdot10^{-1}$	6…2	$<5\cdot10^{-3}$
	Mg, Ca	$1\cdot10^{-4}\ldots1\cdot10^{-2}$	6…2	$<1\cdot10^{-4}$
	Sr	$3\cdot10^{-4}\ldots1\cdot10^{-2}$	2…1	$<2\cdot10^{-4}$
	Ba	$1\cdot10^{-2}\ldots2\cdot10^{-2}$	3	$<5\cdot10^{-3}$
$SrTiO_3$	Ca	$5\cdot10^{-4}\ldots3\cdot10^{-2}$	4…2	$4\cdot10^{-4}$

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-Al_2O_3, $mAl_2O_3\cdot nY_2O_3$ and $mAl_2O_3\cdot nMgO$ 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*-Al_2O_3

Commercially available extra pure γ-Al_2O_3 powders (Donetsk Plant for Chemical Reagents, Ukraine) were used throughout. a-Al_2O_3 was obtained by calcination of ammonia alum at 1200 °C during 3 hours (Chebotkevich, 1975), $Y_3Al_5O_{12}$ was synthesized from Al_2O_3 and Y_2O_3 by calcination at 1200 °C (Neiman et al., 1980). a-Al_2O_3 was powdered in a leucosapphire mortal and sifted through 40, 60, 100 and 160 microns sieves. Particle size of γ -$A1_2O_3$ and $Y_3Al_5O_{12}$ initially was less than 1 μm.
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 Al_2O_3 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-$A1_2O_3$ and $Y_3Al_5O_{12}$.
Effect of a-$A1_2O_3$ 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-Al_2O_3 and 10-12 hours for γ-Al_2O_3 and $Y_3Al_5O_{12}$.

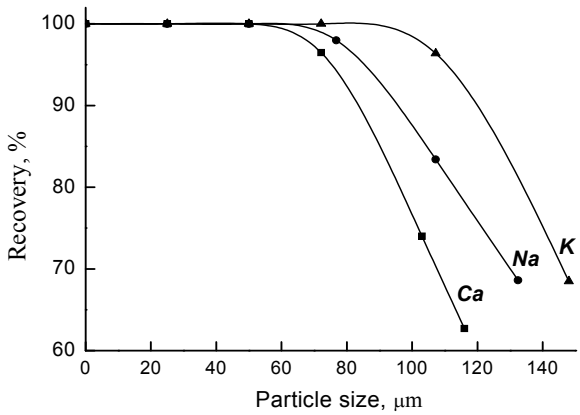

Fig. 7. Effect of a-$A1_2O_3$ particle size on the recovery of Na, K and Ca

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 Al_2O_3 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-$A1_2O_3$ and $Y_3Al_5O_{12}$ 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 ^oC there is a part of unevaporated sulphates of alkali metals in the obtained aluminium oxide. The full decomposition of suphates 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 ^oC 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 A1(OH)3 and hydroxyaluminates (Hanamirova, 1983; Remi, 1973).

Apparently, in aqueous suspensions of $A1_2O_3$ and $Y_3Al_5O_{12}$ 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 a-$A1_2O_3$ and γ-$A1_2O_3$ ($Y_3Al_5O_{12}$), 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 Al_2O_3 and $Y_3Al_5O_{12}$ 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 $A1_2O_3$ and $Y_3Al_5O_{12}$ of different dispersity and for the determination of alkali metals dopants in $A1_2O_3$ charge.

Material	Element	Aqueous extracts			Digestion in condensed phosphoric acid		
		Found, ppm	RSD%	C_{min}, ppm	Found, ppm	RSD%	C_{min}, ppm
α- Al_2O_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_2O_3		14±1	4		14±2	9	
α- Al_2O_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_2O_3		51±3	2		53±4	2	
α- Al_2O_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-Al_2O_3

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-Al_2O_3 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 Al_2O_3 powders. Fractions with particle size less than 40 µm were used throughout. 0.1 g of α-Al_2O_3:Co(Ni) or $mAl_2O_3 \cdot nMgO$:Co(Ni) was mixed with 10 ml of water and 0.2 ml of HNO_3 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, τ =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.

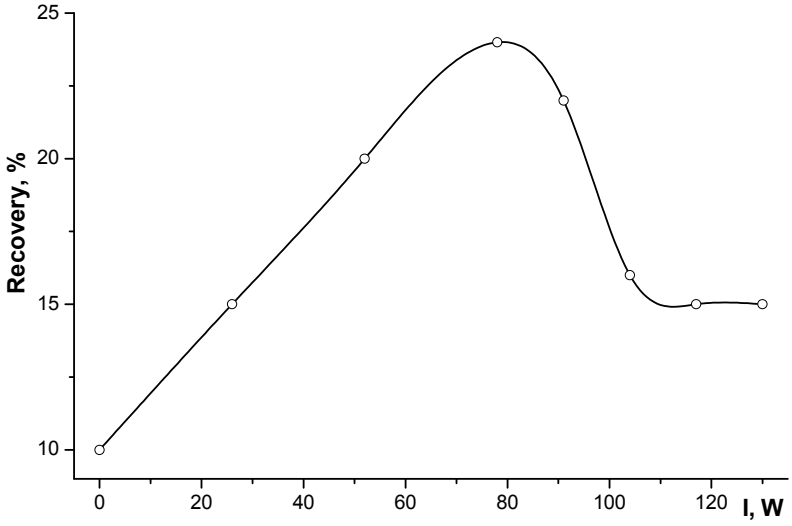

Fig. 8. Dependence of recovery of Co(Ni) on the ultrasonic dispenser driving power (τ =5 min)

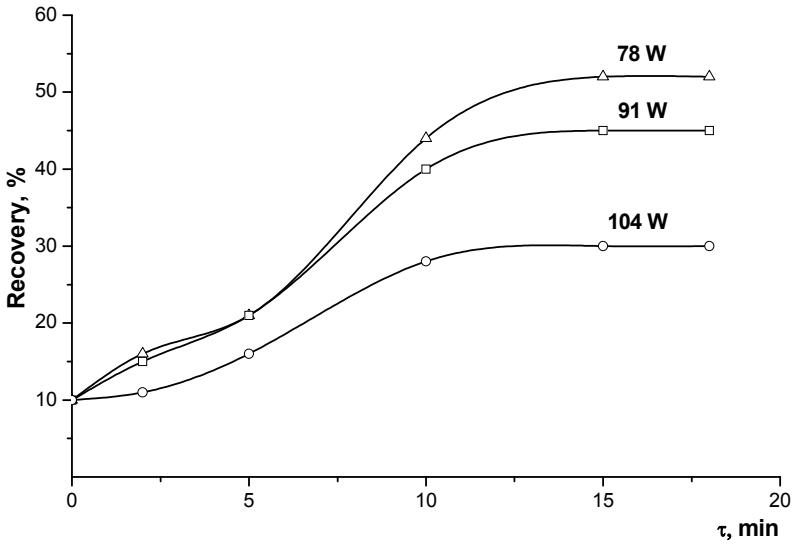

Fig. 9. Dependence of recovery of Co(Ni) on the exposure time

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 α-Al_2O_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.

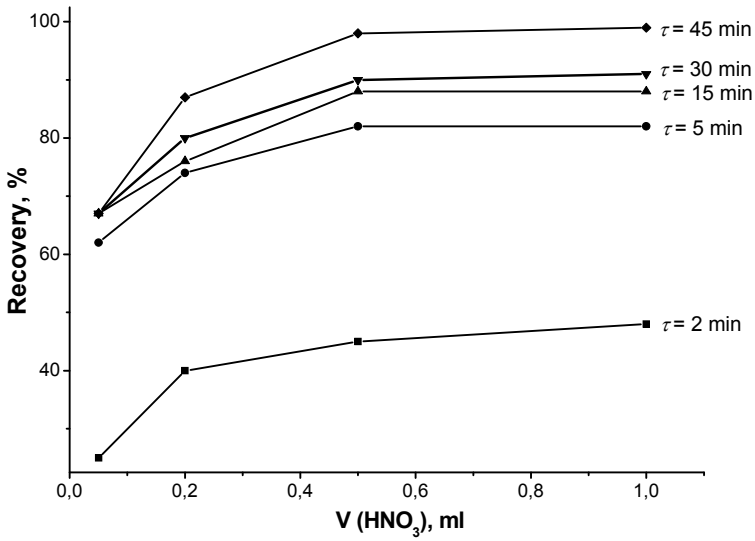

Fig. 10. Dependence of recovery of Co(Ni) on time of exposure and acidity of aqueous suspensions

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_2O_3: Co(Ni)	Ni	800 ± 20	2	10	810 ± 20	4	50
	Co	190 ± 10	4		210 ± 30	5	
$m$$Al_2O_3$ · nMgO: 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 Al_2O_3 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 Al_2O_3 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 us 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 ± 20 990 ± 20	4 2	510 ± 30 1100 ± 50	5 4
Ni	1100 ± 20 2100 ± 40	2 2	1100 ± 50 2200 ± 70	4 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.

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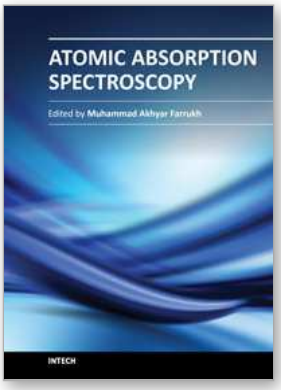

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Atomic Absorption Spectroscopy is an analytical technique used for the qualitative and quantitative determination of the elements present in different samples like food, nanomaterials, biomaterials, forensics, and industrial wastes. The main aim of 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, it's 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.

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