

THE USE OF OPTICAL METHODS OF MEASUREMENT TO INVESTIGATE THE COMPOSITION OF NEW AVIATION MATERIALS

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A procedure for the microwave sample preparation of nickel alloys to determine the mass fractions of Al, Ti, Cr, Co, Nb, Mo, Ru, Ta, W, and Re by atomic-emission spectrometry with an inductively coupled plasma is described. The compositions of the mixtures for solution and the parameters of the microwave dispersion are chosen. The limits of the relative error in measuring the mass fraction of the elements from 0.1% to 20% do not exceed 4% ($P = 0.95$).

Keywords: *microwave sample preparation, nickel alloys, atomic-emission spectrometry with inductively coupled plasma.*

Optical methods are widely used at the present time in analytical laboratories and centers to determine the chemical composition of metal materials. This considerably reduces the time required for the chemical analysis and increases its accuracy.

The ranges of mass fractions of the elements determined in alloys in different bases and metals by mass spectrometry with an inductively coupled plasma (XSeries2) are 10^{-6} –0.1%, atomic-absorption spectroscopy with plasma atomization (240FS) – 0.0001–100% for the transition elements, and atomic-emission spectroscopy with inductively coupled plasma (730ES) – 0.001–100% [1, 2]. Hence, mass spectrometry with an inductively coupled plasma is only used to determine impurities. It is impossible to determine rare-earth and refractory elements in alloys by using atomic-absorption spectroscopy. Atomic-emission spectroscopy with an inductively coupled plasma is the most universal method for determining practically all elements.

We conclude from the above that in a laboratory for carrying out an express analysis it is necessary to use an optical-emission spectrometer with a set of standard samples [3, 4]. To investigate new or nonstandard alloys and materials, it is necessary to use an atomic-emission spectrometer with an inductively coupled plasma. When determining impurities of less than 10^{-4} wt.%, one must use mass spectrometry with an inductively coupled plasma, while gas analyzers must be used to determine gas-forming impurities. The x-ray fluorescence method enables one to carry out a nondestructive analysis of materials and alloys without using standards.

In modern aviation metal research, when developing new deformable and casting heat-resistant alloys, there is a tendency to narrow the limits of the doping range to ensure specified alloy characteristics, which directly depend on its phase composition [5–8]. The phase composition of an alloy, in turn, depends on the chemical composition, and the wider the doping range of the alloy the greater the phase composition varies, and, consequently, the wider the range of values of the characteristics obtained [9–12], in which values not corresponding to the stated values may be obtained. The doping range is narrowed in order to avoid this. For example, in VZhM-type alloys the doping range of Al is 0.5 wt.%, with its content in the

TABLE 1. Effect of the Internal Standard on the Measurement Results

Quantities compared	Element				
	Ti	Fe	Co	Mo	W
Certified value, wt. %	2.53	0.53	15.08	5.50	5.50
Result of the measurements without using the internal standard, wt. %	2.66	0.48	16.11	5.79	5.72
Result of measurements using the internal standard (In), wt. %	2.53	0.51	14.96	5.49	5.51

TABLE 2. Analytical Lines

Element	Analytical line, nm	Interfering element line, nm
Al	257.509	–
Co	238.892; 235.341	V 238.891
Cr	276.259; 206.158	V 276.248; Ru 206.160
Ti	334.188; 337.280	Mo 334.184
Re	197.248; 227.525	W 197.267
Ru	349.894; 379.890	Mo 349.907
Mo	379.825; 202.032	Nb 379.812; Re 202.033
Ta	226.230; 240.063	Nb 226.213; Re 240.074
W	207.912	–
Nb	288.317; 294.154	Mn 294.152

range of 4–6 wt.%, Mo – 0.5% (2–4 wt.%), and Ti – 0.4 wt.% (0.5–2 wt.%) [9]. In new fire-resistant deformable alloys, the doping range of Co is 1.5 wt.%, with its content in the range of 12–20 wt.%, Cr – 1 wt.% (12–20 wt.%), Ti – 0.3 wt.% (1.1–1.4 wt.%), and Nb – 0.4 wt.% (0.5–5 wt.%) [9–11]. To estimate the correspondence of the production of precision heat-resistant alloys, it is necessary to use measurement methods with an error of at least one third of the doping range. In the examples given above, this amounts to 1.5–2.5% relative to the mean value of the mass fraction.

At the All-Russia Research Institute of Aviation Materials, we have developed methods of determining Al, Cr, Co, Re, W, Mo, Ti, B, Si, Ce, Y, Fe, Cu, Mn, P, La, Ru, Ta, and Nb in nickel alloys over a wide range of concentrations by using atomic-absorption spectroscopy with an inductively coupled plasma. These methods have been developed using a Varian 730 ES spectrometer with axial scanning of the plasma. The standard operating parameters of the spectrometer are as follows: plasma power – 1.2 kW, argon flow through the atomizer – 0.75 liters/min, plasma-forming flux – 15 liters/min, additional flux – 1.5 liters/min, stabilization delay – 15 sec, measurement time – 5 sec, number of measurements – 5, and working gas – argon of 99.998% purity. The system for introducing the solutions being analyzed into the spectrometer consists of a Quartz Torch quartz burner for the Varian Axial Chamber, a glass atomizer Twister Spray Chamber, and a SeaSpray Nebulizer 2mL/min glass concentric atomizer. To determine low contents of elements in concentrated solutions (with a hydrofluoric acid content of greater than 0.2%), we used a PolyCon Nebulizer plastic atomizer.

To increase the accuracy of the results of the analysis, we used an internal standard, namely, an additional component introduced in the same amount in all the prepared solutions. By using it, we were able to compensate for the spectrometer drift, partly matrix effects, and also change the size of the drop of aerosol and the rate at which it was fed to the burner, caused, in turn, by the difference in the viscosity between the analyzed and calibrated solutions prepared by standard additions. The element was chosen taking into account the recommendations made in [13]. For nickel alloys, we chose the In 410.176 and Ga 287.419 nm lines. The intensity of the first line was higher, but the Ru and Ce lines are superimposed on it, which leads to incorrect results when these elements are present in the melt. In this case, we use Ga. Experiments using the State

TABLE 3. Results of a Determination of the Elements in the Standard Sample of the Composition of Nickel Alloys ($n = 3, P = 0.95$)

Quantities compared	Element of standard sample				
GSO 1609–79 of the composition of an alloy based on nickel (N15)					
	Cr	W	Mo	Ti	Co
Certified values, wt.%	10.02 ± 0.09	5.50 ± 0.05	5.50 ± 0.04	2.53 ± 0.02	15.08 ± 0.13
Values obtained, wt.%	10.03 ± 0.01	5.47 ± 0.06	5.53 ± 0.06	2.57 ± 0.03	15.02 ± 0.14
GSO 1479–91 P of the composition of an alloy based on XhN62MVKYu (N13b) nickel					
	Cr	W	Mo	Ti	Al
Certified values, wt.%	17.87 ± 0.16	6.49 ± 0.06	4.38 ± 0.04	1.11 ± 0.01	2.86 ± 0.02
Values obtained, wt.%	17.97 ± 0.18	6.35 ± 0.07	4.43 ± 0.05	1.11 ± 0.01	2.89 ± 0.03
GSO 10124–2012 of the composition of the heat-resistance alloy VZhM5U					
	Cr	W	Ta	Re	Co
Certified values, wt.%	3.58 ± 0.03	4.57 ± 0.04	5.08 ± 0.04	4.99 ± 0.05	10.92 ± 0.11
Values obtained, wt.%	3.55 ± 0.04	4.55 ± 0.05	5.16 ± 0.06	4.95 ± 0.06	11.15 ± 0.14

TABLE 4. Results of a Determination of the Mass Fraction of Elements in INCO 625 Alloy When Carrying Out All-Round Tests ($n = 3, P = 0.95$)

Quantities compared	Element						
	Al	Co	Cr	Ti	Fe	Mo	Nb
Certified value, wt.%	0.207 ± 0.014	0.46 ± 0.02	20.99 ± 0.12	0.264 ± 0.012	4.64 ± 0.09	8.86 ± 0.08	3.49 ± 0.05
Result of the measurement, wt.%	0.206 ± 0.003	0.44 ± 0.01	20.95 ± 0.07	0.264 ± 0.002	4.71 ± 0.03	8.92 ± 0.09	3.41 ± 0.05

Standard Sample GSO 1609-79 of alloy composition based on nickel (N15) show a considerable increase in the accuracy of the analysis when using the internal standard (Table 1).

In order to reduce matrix effects when constructing the calibration graphs, we chose the method of standard additions. In this case, we used the standard samples of the solutions of the ions of the elements, and also multielement standard solutions produced by the High-Purity Standards Company (USA).

In Table 2, we show the main and alternative analytical lines chosen in the development of the procedure, and also closely situated lines of interfering elements. When there are interfering elements present, one must use either a fundamental analytical line or an alternative analytical line.

Experiments on dissolved samples of nickel alloys were carried out in the Milestone ETHOS 1 microwave expansion system in PRO 24 liners with a volume of 75 cm³ with an emergency pressure release. The sample was a metal chip selected from the standard [14]. To dissolve the samples, we used a mixture of mineral acids, in which the separate elements in the alloy composition were dissolved: Al, Co, Ni, and Re were dissolved in dilute nitric acid, Cr and Ru were dissolved in hydrochloric acid, and the refractory elements Ti, Zr, Nb, Mo, Ta, and W were dissolved in hydrofluoric acid. All the acids were purified by distillation; sulfuric acid was not used due to its high viscosity and the difficulties involved in purifying it. As a result, we chose mixtures of acids for dissolving the nickel alloys. On the basis of experiments, we also chose the conditions for the microwave sample preparation of the nickel alloys to determine Al, Co, Cr, Ti, Re, Ru, Mo, Ta, W, Nb, and Ni by the AES-ISP method: a sample mass of 0.2–0.5 g, the mixture for the solution was 10 ml of doubly distilled water, 1 ml of HNO₃, and 1 ml of HF; for alloys containing ruthenium, we used for the solution 10 ml of doubly distilled water, 3 ml of HCl, 1 ml

TABLE 5. Indicators of the Accuracy of the Procedure

Element	Range of measured values (mass fraction), %	Accuracy characteristic	
		limits of the relative error $\pm\delta$, %, $P = 0.95$	limit of recurrence r , %, $P = 0.95$, $n = 2$
Al	0.01–25	2	1.5
Co	0.01–0.05	4	1.5
	>0.05 up to 60	2	1.5
Re	0.02–0.05	5	3
	>0.05 up to 15	2	1.5
Ru	0.02–10	3	3
	0.02–0.05	6	3
Ta	>0.05 up to 3	3	3
	>3 up to 10	2	1.5
W	0.01–4	5	3
	>4 up to 20	3	1.5
Cr	0.05–40	3	3
Mo	0.01–1	2	1.5
	>1 up to 20	3	3
Ti	0.01–1	5	3
	>1 up to 5	3	3

of HNO_3 , and 1 ml of HF; for a chromium content of greater than 15 wt.%, the mixture for the solution at the first stage was 5 ml of doubly distilled water, 5 ml of HCl, and 2 ml of HF, and at the second stage we added 1 ml of HNO_3 ; the solution was gradually heated to a temperature of 170°C over a period of 20 min and was held there for 20 min.

We checked the procedure by analyzing different types of State Standard Samples of alloys based on nickel using the above methods. The results are presented in Table 3, where n is the number of parallel measurements on a single sample. In 2012, the laboratory participated in all-round tests carried out by the SNECMA Company (Table 4). The data obtained indicate that there were no systematic errors in the results of the measurements. The procedures have been certified against the standard [15] at the All-Russia Research Institute of Optophysical Measurements (VNIIOFI), and their metrological characteristics are presented in Table 5.

Conclusions. Based on the above experiments, we chose mixtures of acids and the conditions for microwave sample preparation when dissolving nickel alloys to determine Al, Co, Cr, Ti, Re, Ru, Mo, Ta, W, Nb, and Ni by the atomic-emission spectroscopy method with an inductively coupled plasma, and also the main and alternative analytical lines of the elements being determined.

We have developed and tested the procedure for determining the above elements using the method on different types of standard nickel alloys with a relative error in determining the elements of not more than 4% ($\pm\delta$, for $P = 0.95$) for a content of 0.1–20 wt.%.

The procedures have been certified at the VNIIOFI, and certificates have been obtained and introduced into the Federal Information Fund for the Uniformity of Measurements.

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