Development of the method for quantitative determination of impurities content in heat-resistant welded nickel alloys using the atomic-emission spectrometry with inductively coupled plasma

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Abstract. Using AES-ICP new methods have been developed for quantifying the content of impurity elements Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr in the new heat-resistant nickel alloys. To translate the samples into the solution, accelerated techniques were developed using open systems and the microwave system Mars 5. Optimal analytical parameters for determining the elements were chosen. The influence of matrix elements (nickel and chromium) and methods of its elimination were studied. This made it possible to determine the elements in a wide concentration range from 0.0005 to 30% without preliminary separation of the matrix with good metrological characteristics. The relative standard deviation ($S_r$) is 0.05-0.005 at the element content from 1 to 30% and does not exceed 0.20 at the element content from 0.0005 to 0.1%. New method of analytical control was used to correct the processes of melting alloys by vacuum induction melting, compacting capsules and welding process with other heat-resistant alloys, which will ensure the performance of work on the improvement of metal compounds in liquid rocket engines.

1. Introduction

The processes of melting alloys by vacuum induction melting, compacting, subsequent processes of VDP and ELP, heat treatment, welding process with other heat-resistant alloys requires verification of the homogeneity of the received materials and welds [1]. For this purpose, it is necessary to systematically carry out elemental analysis of a large number of samples both for the main alloying components (Cr, Ti, Al, Mo, Nb, Ta, W), and for microalloying additives and impurities (Hf, Si, Mn, Fe, Mg, B, Ce, Cu, Zr). The absence of a set of standard samples of the composition of heat-resistant nickel alloys to determine this list of impurity elements limits the choice of the method of analysis.

The optimal research method for solving these problems is the atomic emission spectrometry with inductively coupled plasma (AES-ICP), which allows to simultaneously determine a large set of elements of different concentrations. The influence of nickel and chromium on the definition of Al, B,
Ce, Co, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr has been little studied [2] and is often absent in the literature.

2. Experimental results

AES-ICP was used for our research. The method is the most perspective for determination of the elements, regarding sensitivity, selectivity and metrological characteristics [3, 4]. Work was conducted on the plasma spectrometer of ULTIMA 2 firms "HORIBA JOBIN YVON" (France-Japan). The optimal analytical parameters for the simultaneous determination of the above listed chemical elements were experimentally found: the discharge power – 1.2 kW; cooling argon flow is 14 l/ min; transporting is 0.80 l/min; plasma is 0.5 l/min; observation height 15 mm above the top turn of the induction coil; the speed rate samples is 1.0 ml/min. Analytical lengths of waves were chosen for determination of the elements, that provide the suitable detection limits, a minimum of adjustments for background and overlapping of spectral lines [5]. Optimal analytical lengths of waves are presented in tables 1.

The detection limits of the elements were estimated [6]. In table 1, the calculated detection limits of elements are presented. It is seen that the detection limits on the background 1000 ppm of nickel and 500 ppm of chromium are significantly different from those in the pure solutions and not for the better.

| № | Element | Length wave, λ nm | Detection limit, ppb (3σ) | Intensity |
|---|---------|------------------|--------------------------|-----------|
|   |         |                  | in pure solution         | on the background 2000 ppm Ni | on the background 500 ppm Cr |        |
| 1 | Al      | 396,152          | 0.3                      | 1.8        | 1.2        | 64000 |
| 2 | B       | 208,959          | 0.2                      | 1.9        | 1.6        | 74000 |
| 3 | Ce      | 413,765          | 0.6                      | 3.9        | 2.6        | 15700 |
| 4 | Co      | 228,616          | 0.4                      | 2.5        | 2.0        | 11000 |
| 5 | Cr      | 267,716          | 0.2                      | 1.8        |           | 75500 |
| 6 | Cu      | 324,754          | 0.2                      | 2.2        | 1.9        | 95000 |
| 7 | Fe      | 259,940          | 0.2                      | 2.0        | 1.8        | 89000 |
| 8 | Hf      | 282,022          | 0.2                      | 2.5        | 1.9        | 52000 |
| 9 | Mg      | 279,553          | 0.03                     | 0.5        | 0.4        | 105000 |
| 10| Mn      | 257,810          | 0.05                     | 0.7        | 0.8        | 98600 |
| 11| Mo      | 280,775          | 0.2                      | 1.8        | 1.9        | 98000 |
| 12| Nb      | 316,340          | 0.3                      | 3.8        | 2.2        | 16800 |
| 13| Ni      | 221,647          | 0.2                      | 1.5        |           | 28000 |
| 14| Si      | 251,611          | 1.3                      | 4.0        | 3.0        | 92000 |
| 15| Sn      | 189,989          | 6                        | 19         | 18         | 9800 |
| 16| Ta      | 363,558          | 0.6                      | 3.6        | 1.7        | 15100 |
| 17| Ti      | 334,941          | 0.1                      | 1.8        | 1.5        | 150000 |
| 18| V       | 292,402          | 0.2                      | 1.9        | 1.4        | 125000 |
| 19| W       | 207,911          | 0.4                      | 3.2        | 1.8        | 28600 |
| 20| Zr      | 339,198          | 0.2                      | 2.5        | 2.4        | 49900 |

The main problem of emission analysis is to take into account the influence of the matrix (basis). The influence of matrix elements (nickel and chromium) and methods of their removal were studied. An increase in the concentration of matrix elements to 200 ppm did not affect the analytic signals of the impurity elements, when they were more than 10 ppb. With an increase in the concentration of Ni or Cr in the solution a change in the slope of the calibration curves and a shift was observed (figure 1, 2). It is particularly difficult to determine the elements near the limits of their detection against the
background of complex matrices. In figure 1, 2 the calibration graphs of Co and Nb are presented for pure solutions, containing 500 ppm Cr or 2000 ppm Ni. It can be seen, that at concentration of Co and Nb below 10 ppb, there is a distortion of the calibration curves and, consequently, a deterioration in the metrological characteristics of the determination of the elements. When determining the elements near the limits of their detection (5 ppb), other impurity elements (at a content of more than 100 ppm) begin to affect their analytical signals. Allowable relations of the nickel matrix element to the determined elements are presented in table 2. To eliminate the matrix interference due to the changing concentration of the matrix element, the method of interactive concordance of matrix [4] has been applied.

Significant factor is the choice of the concentration of the matrix element in the solution, which is not violated to the stability of work of the system burner - nebulizer. For chromium favorable is a concentration no more than 1000 ppm and for a nickel - 2000 ppm.

![Figure 1](image1.png)

**Figure 1.** Calibration graphs of cobalt in pure solution (a) and on the background 500 ppm Cr (b).

![Figure 2](image2.png)

**Figure 2.** Calibration graphs of niobium in pure solution (a) and on the background 2000 ppm Ni (b).
Table 2. Allowable relations of the nickel matrix element to the determined elements.

| №  | Element | Length wave, λ, nm | Allowable relations | The interval of determined concentrations of element (ppb) | The relative standard deviation (S_r) |
|----|---------|------------------|-------------------|------------------------------------------------|-----------------|
| 1  | Al      | 396,152          | 1∙10^6            | 10-10000                                                    | 0,15-0,01       |
| 2  | B       | 208,959          | 1∙10^5            | 5-10000                                                     | 0,15-0,02       |
| 3  | Ce      | 413,765          | 2∙10^5            | 15-10000                                                    | 0,20-0,01       |
| 4  | Co      | 228,616          | 6∙10^5            | 10-10000                                                    | 0,15-0,01       |
| 5  | Cr      | 267,716          | 1∙10^6            | 2-10000                                                     | 0,15-0,005      |
| 6  | Cu      | 324,754          | 1∙10^5            | 5-10000                                                     | 0,10-0,004      |
| 7  | Fe      | 259,940          | 2∙10^5            | 8-10000                                                     | 0,10-0,005      |
| 8  | Hf      | 282,022          | 5∙10^4            | 5-10000                                                     | 0,15-0,01       |
| 9  | Mg      | 279,553          | 2∙10^6            | 1-10000                                                     | 0,15-0,006      |
| 10 | Mn      | 257,810          | 1∙10^6            | 2-10000                                                     | 0,10-0,005      |
| 11 | Mo      | 280,775          | 2∙10^5            | 6-10000                                                     | 0,15-0,006      |
| 12 | Nb      | 316,340          | 1∙10^5            | 9-10000                                                     | 0,18-0,01       |
| 13 | Si      | 251,611          | 6∙10^5            | 8-10000                                                     | 0,15-0,01       |
| 14 | Sn      | 189,989          | 1∙10^5            | 12-10000                                                    | 0,14-0,01       |
| 15 | Ta      | 363,558          | 3∙10^5            | 8-10000                                                     | 0,15-0,01       |
| 16 | Ti      | 334,941          | 1∙10^6            | 5-10000                                                     | 0,20-0,005      |
| 17 | V       | 292,402          | 1∙10^5            | 10-10000                                                    | 0,18-0,007      |
| 18 | W       | 207,911          | 3∙10^5            | 12-10000                                                    | 0,15-0,009      |
| 19 | Zr      | 339,198          | 1∙10^6            | 2-10000                                                     | 0,12-0,008      |

The influence of the nature and concentration of various acids on the analytical signals of elements were studied. On figures 3-5 the dependences of analytical signals of elements from concentration of HCl, H_2SO_4, H_3PO_4 acid in the analyzed solution are shown. As follows from experimental data, changes in concentration of acid in the analyzed solution lead to changes in analytical signal, and the degree of change depends on the nature and concentration of acid. Hence, a solution of 2M HCl decreases the analytical signal Nb on 3%, while the sulfuric acid of the same concentration by 20%. The increase in the concentration as HCL and HNO_3, from 0.01 M to 1 M changed analytical signals of the elements not more than by 10%. Significant influence on the analytical signals of the elements renders the changed concentrations of phosphoric and sulfuric acids in solution. The best analytical medium is hydrochloric acid. However, the practical error can be avoided by maintaining an adequate acid content in tests and standard solutions. Uncontrolled fluctuations in the concentration of acids, especially sulphuric, can lead to errors which are significantly greater than instrumental.
Figure 3. The dependence of the intensity of the signal elements from concentration of hydrochloric acid.

Figure 4. The dependence of the intensity of the signal elements from concentration of sulfuric acid.
Figure 5. The dependence of the intensity of the signal elements from concentration of phosphoric acid.

Table 3. Methods of dissolution of heat-resistant nickel alloys.

| Composition of samples | Reagents for dissolution | Dissolution conditions | Reagents for retention of matrix and determinable elements in solution | Determinable elements | Method of analysis (found impurity content) |
|------------------------|--------------------------|------------------------|---------------------------------------------------------------------|----------------------|--------------------------------------------|
| Ni 70-90%              | HF + HNO₃ + HCl          | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| Cr 10-20%              | HF                       | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| Co 0.01-15%            | H₂SO₄ + HCl              | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| Mo 0.01-15%            | H₂SO₄ + HCl              | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| W 0.1-15%              | H₂SO₄ + HCl              | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| Nb 0.1-5%              | (NH₄)₂SO₄                 | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| Al 0.1-5%              | (NH₄)₂SO₄ + H₂SO₄         | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| V 0.01-3%              | H₂SO₄ + HCl              | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
| Ti 0.01-3%             | H₂SO₄ + HCl              | Heating in Pt, teflon, glass-carbon dishes (from 50 minutes to 5 hours) | H₃PO₄ + HCl (2-4M)                                               | Al, B, Ce, Co, Cr, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr | AES-ICP (10⁻³·n·10%)                       |
To perform elemental analysis using AES-ICP method, it is necessary to transfer the analyzed samples to a solution. The studied materials heat-resistant nickel alloys are rather complex objects of investigation because of the difficulties of transferring the samples to solution and obtaining stable solutions of high concentrations of readily hydrolyzed elements of tungsten, niobium, titanium, molybdenum, tantalum, zirconium, and hafnium. Mineral acids and their mixtures of different concentration were used for dissolution [7]. Optimal schemes for sample dissolution and methods of retaining elements in solution have been found (table 1). Dissolution was carried out with a mixture of nitric, hydrochloric and hydrofluoric acids. To prevent the precipitation of tungsten salts, H$_3$PO$_4$ was added. After dissolving the samples and removing hydrofluoric acid, the residues were transferred with 2M HCl to volumetric flasks. Such a high concentration of acid is necessary for obtaining stable solutions of readily hydrolyzed elements. The solutions obtained were diluted 5-10 times with 1 M HCl before measurement on the plasma spectrometer. To accelerate the decomposition of the samples, modern systems were used: the microwave mineralizer Minotaur-2 (Russia) and the autoclaved microwave system MARS 5 (CEM Corporation, USA). The most effective dissolution was achieved using the MARS 5 module. The larger samples dissolve in fewer reagents and in a shorter period of time. Sample weighed 100 mg completely dissolved in 10 minutes in a mixture of concentrated nitric, chloric and hydrofluoric acids at a temperature of 210°C.

To determine silicon, this method of sample preparation is not suitable. Therefore, the wet-fusion method [7] was also used: heating samples in a mixture of H$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ (until a clear melt). Method allows to dissolve many difficult compound being uncovered (table 3). At the same time, blank experiments were conducted to control the purity of the reagents. All reagents used were of the high purity.

Samples were analyzed with respect to developed programs. To confirm the correctness of the results of the determination of the elements, they were compared with the data of other analytical methods: atomic absorption spectrometry (AAS) and atomic emission spectrometry with a glow discharge (AES-GD), as well as with certified passport contents of standard samples of nickel alloys. The results of the analysis of the samples are shown in tables 4, 5. Good convergence of the results of the determination of elements by different methods is obtained. The developed new methods for determining the elements favorably differ from the previously proposed expressiveness, the ability to simultaneously determine a large set of elements in a wide range of concentrations from 0.0005 to 30% with good metrological characteristics without preliminary separation of the matrix and without using solid standard samples. The relative standard deviation ($S_r$) is 0.05-0.005 at the content of elements from 1 to 30% and does not exceed 0.20 at the elements content from 0.0005 to 0.1%.

Table 4. The results of the determination of element contents in heat-resistant nickel alloys, obtained by different methods (n=3, P=95).

| Determinable elements | Sample No | Found mass contents of the elements, % |
|-----------------------|-----------|---------------------------------------|
|                       |           | AES-ICP | $S_r$ | AES-GD or AAS | $S_r$ |
| Al                    | 1         | 2.13    | 0.04 | 2.09         | 0.04 |
|                       | 2         | 4.08    | 0.02 | 4.02         | 0.02 |
|                       | 3         | 4.41    | 0.02 | 4.45         | 0.02 |
| Co                    | 1         | 0.030   | 0.09 | 0.032        | 0.09 |
|                       | 2         | 13.61   | 0.008| 13.54        | 0.008|
| Element | Measurement | Measurement | Measurement | Measurement |
|---------|-------------|-------------|-------------|-------------|
| Cr      | 16.63       | 0.006       | 16.56       | 0.006       |
|         | 10.30       | 0.007       | 10.35       | 0.007       |
|         | 9.71        | 0.005       | 9.79        | 0.005       |
|         | 0.010       | 0.13        | 0.011       | 0.13        |
| Cu      | 0.012       | 0.12        | 0.012       | 0.12        |
|         | 0.011       | 0.12        | 0.010       | 0.12        |
|         | 1.07        | 0.05        | 1.03        | 0.05        |
| Fe      | 0.64        | 0.06        | 0.67        | 0.06        |
|         | 0.32        | 0.06        | 0.31        | 0.06        |
|         | 0.14        | 0.07        | 0.14        | 0.07        |
| Mn      | 0.073       | 0.08        | 0.071       | 0.08        |
|         | 0.021       | 0.09        | 0.020       | 0.09        |
|         | 4.09        | 0.015       | 4.05        | 0.015       |
| Mo      | 4.63        | 0.015       | 4.69        | 0.015       |
|         | 8.85        | 0.006       | 8.93        | 0.006       |
|         | 2.52        | 0.018       | 2.59        | 0.018       |
| Nb      | 0.084       | 0.05        | 0.081       | 0.05        |
|         | 0.063       | 0.06        | 0.060       | 0.06        |
|         | 0.024       | 0.07        | 0.021       | 0.07        |
| Sn      | 0.050       | 0.06        | 0.052       | 0.06        |
|         | 0.15        | 0.05        | 0.15        | 0.05        |
|         | 1.12        | 0.01        | 1.13        | 0.01        |
| Ti      | 1.76        | 0.01        | 1.73        | 0.01        |
|         | 0.053       | 0.03        | 0.051       | 0.03        |
|         | 1.16        | 0.04        | 1.13        | 0.04        |
| V       | 0.40        | 0.05        | 0.41        | 0.05        |
|         | 0.035       | 0.08        | 0.032       | 0.08        |
|         | 1.27        | 0.04        | 1.23        | 0.04        |
| W       | 5.16        | 0.02        | 5.23        | 0.02        |
|         | 5.03        | 0.02        | 5.08        | 0.02        |
|         | 0.0016      | 0.11        | 0.0019      | 0.11        |
| Zr      | 0.023       | 0.07        | 0.020       | 0.07        |
|         | 0.30        | 0.03        | 0.31        | 0.03        |
### Table 5. The results of determining of element contents in standard samples of the composition (SSC) of nickel alloys, obtained by various methods (n=10, P=95).

| SSC No | Determinable elements | AES-ICP | AAS | AES-GD | Certified passport contents |
|--------|------------------------|---------|-----|--------|----------------------------|
| H10a   | Fe                     | 0.43±0.02 | 0.40±0.01 | 0.45±0.04 | 0.41±0.02                 |
|        | Mn                     | 0.23±0.01 | 0.24±0.009 | 0.20±0.03 | 0.238±0.009               |
|        | Mo                     | 27.1±0.1  | 26.9±0.15 | 27.3±0.2 | 27.05±0.10                |
| 9-82п  | Ti                     | 0.084±0.003 | 0.080±0.005 | 0.090±0.010 | 0.086±0.005          |
|        | V                      | 1.61±0.07 | 1.54±0.08 | 1.67±0.10 | 1.57±0.08                |
|        | Si                     | 0.085±0.005 | 0.094±0.008 | 0.089±0.006 |
| 167-a  | Al                     | 0.76±0.01 | 0.79±0.02 | 0.82±0.05 | 0.77±0.01                |
|        | Cr                     | 20.60±0.09 | 20.78±0.09 | 20.55±0.10 | 20.70±0.06              |
|        | Cu                     | 0.024±0.06 | 0.029±0.04 | 0.021±0.08 | 0.028±0.05              |
|        | Mn                     | 0.26±0.01 | 0.25±0.01 | 0.22±0.04 | 0.26±0.02                |
|        | Ti                     | 2.74±0.06 | 2.61±0.08 | 2.58±0.09 | 2.68±0.06                |
|        | Si                     | 0.45±0.02 | 0.40±0.04 | 0.43±0.02 |
| 296    | Al                     | 1.20±0.04 | 1.29±0.06 | 1.16±0.09 | 1.24±0.01                |
|        | Cr                     | 18.4±0.1 | 18.6±0.1 | 18.4±0.1 | 18.51±0.01              |
|        | Fe                     | 0.50±0.01 | 0.49±0.006 | 0.48±0.02 | 0.497±0.003            |
|        | Mn                     | 0.12±0.005 | 0.13±0.005 | 0.13±0.01 | 0.132±0.002             |
|        | Mo                     | 10.0±0.05 | 10.2±0.1 | 10.2±0.1 | 10.09±0.002             |
|        | Ti                     | 2.54±0.04 | 2.63±0.07 | 2.50±0.09 | 2.59±0.01               |
|        | W                      | 4.49±0.08 | 4.34±0.09 | 4.42±0.01 |
|        | Si                     | 0.36±0.01 | 0.37±0.03 | 0.346±0.002 |
| 238    | Co                     | 0.0071±0.0005 | 0.0074±0.0004 | 0.0082±0.0009 | 0.0076±0.0004 |
|        | Cu                     | 0.10±0.01 | 0.11±0.009 | 0.14±0.03 | 0.11±0.01               |
|        | Fe                     | 0.11±0.01 | 0.12±0.01 | 0.14±0.02 | 0.12±0.009              |
|        | Mg                     | 0.007±0.001 | 0.009±0.002 | 0.010±0.009 | 0.008±0.001          |
|        | Mn                     | 0.17±0.009 | 0.18±0.008 | 0.19±0.01 | 0.18±0.008              |
|        | Si                     | 0.09±0.01 | 0.12±0.02 | 0.10±0.01 |
3. Conclusions
Using the method AES-ICP, new express methods of analysis of heat-resistant nickel alloys were developed:

1. New methods for rapid dissolution of samples, using the microwave system Mars 5, were developed.

2. The optimal composition of acids $2\text{M HCl} + \text{H}_3\text{PO}_4$ (without the use of hydrofluoric acid) was chosen for long-term storage of solutions (retention in solutions of refractory elements) for their subsequent use as reference samples to establish the reproducibility of the technological process.

3. The proposed methods allowed to determine the content of elements: Al, B, Ce, Co, Cu, Hf, Fe, Mg, Mn, Mo, Nb, Si, Ta, Ti, W, V, Zr beginning from $5 \times 10^{-3}\%$ and above without prior separation of matrix and without using solid standard samples with good metrological characteristics. The relative standard deviation ($S_r$) is $0.05$-$0.005$ at the content of elements from 1 to 30% and does not exceed 0.20 at the elements content from 0.0005 to 0.1%.

4. New methods of analytical control were used to correct the processes of alloying by vacuum induction melting method, compaction of capsules and welding process with other high-temperature alloys, which will allow performing work on improving metal compounds in liquid rocket engines.

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