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THE ROLE OF ANALYTICAL DIAGRAMS IN THE PREPARATION OF METHODICAL PROCEDURES IN MODERN, CHEMICAL RESEARCH LABORATORIES

ROLA DIAGRAMÓW ANALITYCZNYCH W PRZYGOTOWANIU PROCEDUR METODYCZNYCH W NOWOCZESNYCH, CHEMICZNYCH LABORATORIACH BADAWCZYCH

***Summary**: In correctly functioning chemical research laboratories, employing GLP (Good Laboratory Practice) principles, especially in accredited laboratories or those ones applying for the accreditation certificate, it is necessary – apart from the development of the policy of quality and systemic procedures – to prepare the methodological (analytical) procedures in a form, being consistent and comprehensible for the laboratory staff. The analytical diagrams, developed in a synthetic and transparent form, are a significant factor in the mentioned documents. In the present paper, the methods of constructing the analytical diagrams in the field of the studies on testing and materials for the determination of chemical composition of the isolated intermetallic γ' phases, when applying the technique of atomic absorption spectrometry (AAS), exposing the element form in the first case and a complex form with consideration of the specified dilutions of the analyzed samples (comprehensive analytical diagram) in the second case.*

***Keywords**: analytical diagrams, isolates of γ' phase, atomic absorption spectrometry (AAS)*

***Streszczenie**: W prawidłowo funkcjonujących chemicznych laboratoriach badawczych stosujących zasady GLP – Good Laboratory Practice, zwłaszcza w laboratoriach akredytowanych lub ubiegających się o certyfikat akredytacji, oprócz opracowania polityki jakości i procedur systemowych, konieczne jest również przygotowanie w zwartej i zrozumiałej dla personelu laboratoryjnego formie, procedur metodycznych (analitycznych). Istotnym czynnikiem w tych dokumentach są opracowane w syntetycznej i przejrzystej postaci diagramy analityczne. W niniejszej pracy przedstawiono sposoby konstruowania diagramów analitycznych w obszarze badań materiałoznawczych, do określania składu chemicznego wyizolowanych faz międzymetalicznych γ', stosując technikę atomowej spektrometrii absorpcyjnej [ang. atomic absorption spektrometry] (AAS), eksponując w pierwszym przypadku formę pierwiastkową, a w drugim kompleksową z uwzględnieniem konkretnych rozcieńczeń roztworów próbek analizowanych (ang.comprehensive analytical diagram).*

***Słowa kluczowe**: diagramy analityczne, izolaty fazy γ', atomowa spektrometria absorpcyjna (AAS)*

Introduction

The increasing requirements connected with the integration with the European Union structures and stronger and stronger competition on the domestic market, including also that one between the research units, have brought about the necessity of guaranteeing the high quality of the performed tests and reliability of the obtained results by the research laboratories [1–3]. General requirements concerning the competences of the research and calibration laboratories cause that it becomes necessary to systematize the basic activities connected with the development and introduction of quality system in the field of research laboratories' management. The discussed topic is very complicated as it covers the management of the lab resources as well as the technical competences. The mentioned competences should be referred in particular to the laboratory staff and, more precisely to its qualifications and preparation to perform the specified tests or determinations, to laboratory rooms, satisfying the appropriate requirements for running the discussed tests, to the laboratory equipment with the analytical instruments and control-measuring devices and in the auxiliary equipment in respect of preparing the delivered samples to tests. Use of chemical reagents and standards, possessing the necessary certificates, the laboratory glassware of the appropriate grade etc. and, what is very important, development of the appropriate analytical methods together with their validation [4–11]. The mentioned areas of technical competences of the research laboratories constitute simultaneously the most important GLP (Good Laboratory Practice) principles.

In the present paper, when referring to the methodology of the tests, the methods of constructing the analytical diagrams in the extremely difficult area of the studies on testing and materials i.e. for determination of chemical composition of the inter-metallic γ' phase isolates with the application of atomic absorption spectrometry, have been presented [11–15].

Short characteristic of γ' phase

The creep resistance of multi-component nickel alloys is mainly determined by the presence of γ' phase, due to a complex of its very specific properties [15]. The choice of the chemical composition of the creep-resistant nickel-based alloys determines the amount of the γ' phase precipitates. In many cases, the volume fraction of the γ' phase precipitates in the structure of nickel superalloys is up to 68%. Depending on the amount of alloying constituents added to nickel alloys and their final content in these alloys, and on the applied variant of alloy heat treatment, the chemical composition of the γ'-Ni_3(Al, X) phase, where X = Ti, Ta, Nb, can vary in a very wide range of values. This is due to the fact that cobalt can replace nickel, while titanium, niobium and tantalum can occupy the position of aluminium in the ordered γ' phase lattice. Molybdenum, chromium and iron can replace both aluminium and nickel in the Ni_3Al compound [15]. Typically, in the precipitates of γ' phase, the content of from five to ten metal elements is determined.

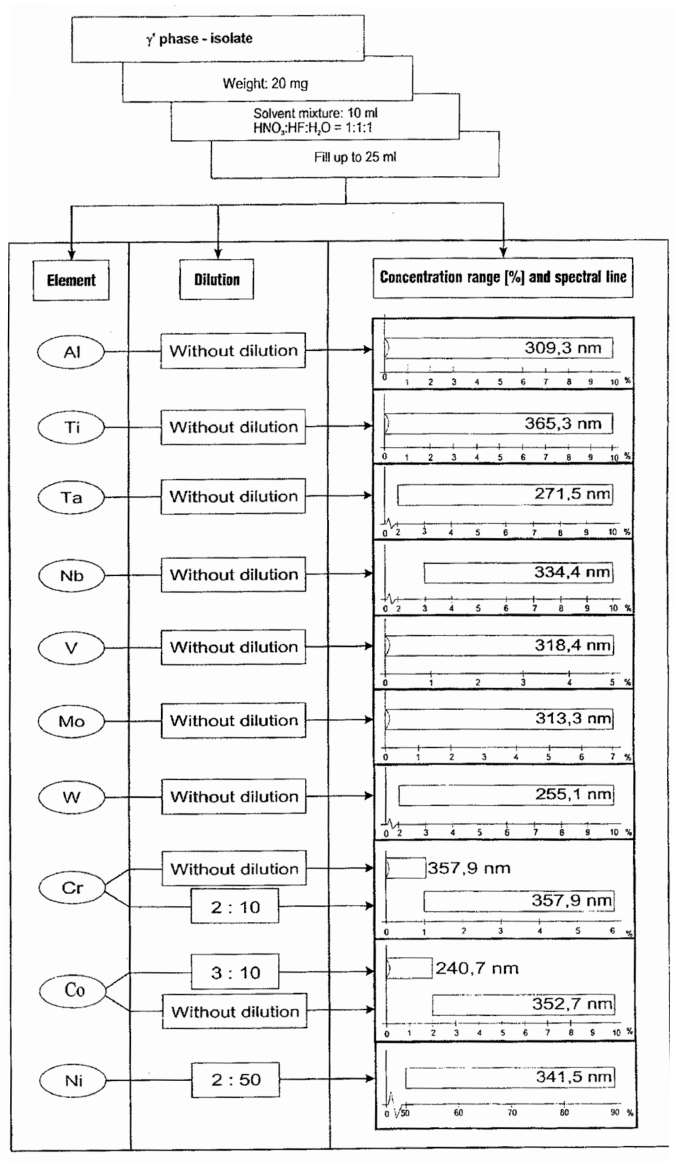
The ways of constructing the analytical diagrams

A high number of the grades of multi-component alloys on the basis of nickel and their comprehensive and widely varying chemical composition determine the chemical composition of the intermetallic γ' phase isolates. Hence, it is difficult to specify univocally the ranges of occurrence of the particular components in the γ' phase isolates. The following intervals of the concentration of the elements, as present in the γ' phase composition, have been adopted with a certain approximation:

Al – up to 10%,
Ti – up to 10%,
Nb – from 3 to 10% (Fig. 2 illustrates even the range from 2%),
Ta – from 2 to 10%,
Co – up to 10%,
Cr – up to 6%,
Mo – up to 7%,
V – up to 5%, and
W – from 2 to 10%.

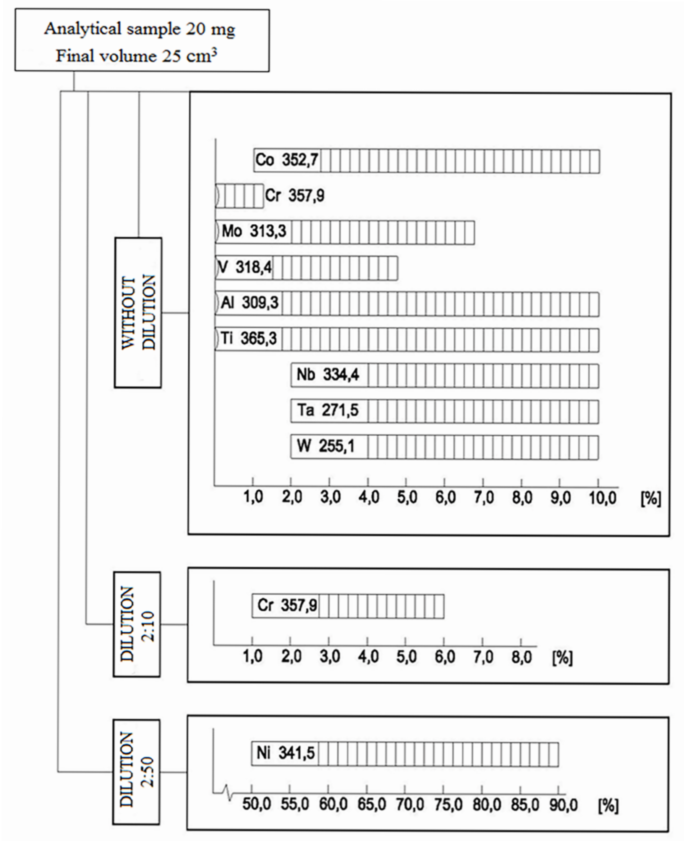
To determine the content of the particular metallic elements, the technique of atomic absorption spectrometry (AAS) was chosen. The choice of the mentioned above method (AAS) was performed based upon its numerous advantages, including, *inter alia*, sensitivity of determinations, selectivity, accuracy and precision. When commencing the preparation of the analytical diagrams, it was considered that in the γ' phase isolates, the contents of 5–10 metallic elements, occurring in relatively wide range of concentrations, should be determined; therefore, the discussed schemes contained such date as weighing of the sample (isolate), final volume of the sample's solution, size of the necessary dilutions and the employed analytical lines together with the corresponding concentration ranges. Two types of the analytical diagrams were developed; they are presented in Fig. 1 and 2. The both discussed diagrams were performed with the consideration of the same concentration ranges of the particular metallic elements, present in the composition of γ' phase isolates. The analytical diagram of the elements, as shown in Fig. 1 was developed when assuming the method for determination of the particular elements, occurring in the γ' phase isolates as the initial point. On the other hand, the complex analytical scheme, as illustrated in Fig. 2 was performed when basing on the thoroughly calculated variants of the dilutions of the sample solutions (γ' phase isolates) and the employed spectral lines. The transparency of the both analytical diagrams is their common and significant feature which enables a quick and appropriate decision of the laboratory staff in relation to the selected effective method of analytical procedure, depending on the expected chemical composition of the analyzed γ' phase isolates. Apart from the analytical schemes, the analytical procedure should contain the method for preparation of the samples and standard solutions.

Fig. 1. Analytical diagram for the analysis of γ' phase isolates by AAS method



Source: own development.

Fig. 2. The comprehensive analytical diagram for determination of γ' phase chemical composition by AAS technique [15]



Preparation of samples (isolates) and standards

Chemical composition of the γ' phase precipitates is determined during analysis of the γ' phase isolates. Various reagents and extraction conditions are used to isolate and extract the γ' phase from multi-component nickel alloys [11-15]. In studies carried out at the Silesian University of Technology [54,56], the γ' phase was isolated by anodic dissolution in a reagent containing 20 ml $HClO_4$, 50 ml HNO_3, 1000 ml CH_3OH, at a current density of 0.1 A/cm^2 and temperature ranging from 0 to 5°C.

The method of determining the content of metallic elements in the γ' phase isolates using atomic absorption spectrometry was described in detail in [11-15]. The 20 mg weighed portion of the isolate was placed in a 100 ml Teflon beaker, adding 10 ml of the digesting mixture (HNO_3: HF: H_2O = 1: 1: 1) and heating the whole gently on a heating plate until complete dissolution of the isolate. Then 10 ml of HCl were added and the contents of the beaker were carefully evaporated to dryness. This operation was repeated to determine cobalt content in the γ' phase isolate. The beaker walls were then rinsed with a small amount of water and 2 ml of concentrated hydrochloric acid and 1 ml of concentrated hydrofluoric acid were added. The solution was heated to dissolve the salt, boiled, cooled to room temperature and transferred quantitatively to a 25 ml graduated flask. Then 0.2 g of ammonium fluoride was added, water was added to the mark and the whole was mixed thoroughly.

Taking into account numerous inter-element effects that occur during analysis of γ' phase isolates [15], synthetic standard reference solutions were prepared in parallel with isolate samples by adding varying amounts of base standard reference solutions of all determinants occurring in γ' phase to cover the expected concentrations of these elements. The total mass of metals in each reference standard should be constant and equal to 20 mg. To maintain the same conditions during preparation of standard reference solutions, the order of the individual operations must be the same as when preparing the test sample solutions, i.e. evaporating with hydrochloric acid, adding a certain amount of hydrofluoric acid and ammonium fluoride, and supplementing with water to 25 ml. The blank samples were all reagents used in the analysis. The detailed measuring parameters for the determined elements are given in Tab. 1.

Table 1. Operating parameters

Element	Measuring range %	Analytical Line, nm	Slit, nm	Flame	Type of flame[1]	Burner height, mm	Lamp current, mA[2]	Integration period s	Linear working range, µg/cm^3	Supplementary information
Cr	5-40	357,9	0,7	C_2H_2-N_2O	R	8	25	3	10	
Co	0-30	240,7 352,7	0,2	C_2H_2-Air C_2H_2-N_2O	U	5	30	3	6 500	
Al.	0,5-7	309,3	0,7	C_2H_2-N_2O	R	6	25	3	80	
Ti	0-5	365,3	0,2	C_2H_2-N_2O	R	6	36	3	150	add. $AlCl_3$ to 1000 µg Al/cm^3
Mo	0-12	313,3 317,0	0,7	C_2H_2-N_2O	R	7	30	3	60 80	
Nb	0,5-7	334,4	0,2	C_2H_2-N_2O	R	5	36	10	900	
Ta	0,5-6	271,5	0,2	C_2H_2-N_2O	R	5	36	10	1000	add. 0,1 M NH_4F
W	0-11	255,1 400,9	0,2 0,7	C_2H_2-N_2O	R	7	36	10	1400 500	
V	0-2	318,4	0,7	C_2H_2-N_2O	R	6	36	3	100	add. $AlCl_3$ to 1000 µg Al/cm^3

[1] R – reducing, O – oxidizing [2] Lamps Intensitron

Summing up

The both discussed diagrams contain the same amount of information, however being presented in somewhat different graphic form, necessary for the correct choice and correlation of the analytical parameters, serving for determination of the content of the particular elements in intermetallic γ' phase isolates, with the application of atomic absorption spectrometry. The detailed results of chemical analyses of γ' phase isolates are found in the papers [11–15]. When taking into consideration the problem range of the present article, it does not seem purposeful to cite them again. It should be stressed that the use of the so-prepared analytical diagrams by the laboratory staff makes the work in the laboratory throughout the whole measuring cycle decidedly more systematized; it allows also avoiding the unnecessary losses of time for additional calculations with the aim to prepare correctly the dilutions of the samples' solutions as well as to make the appropriate choice of spectral lines [15, 16]. They may be also helpful in the appropriate preparation of synthetic standard solutions in order to calibrate the absorptiometer (photocolorimeter). Additionally, the analysis of the specified quantitative data, as contained in the developed analytical diagrams, facilitates considerably the performance of the validation of the employed analytical method.

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