Chemistry

OPERATING PARAMETERS OF ATOMIC ABSORPTION SPECTROSCOPY FOR QUANTITATIVE DETERMINATION OF CHROMIUM IN CROME ORES, CROME CONCENTRATES AND TAILINGS

A. V. MANUKYAN [1,2*], R. S. HARUTYUNYAN [1**]

[1] *Chair of Inorganic Chemistry YSU , Armenia*
[2] *"Lernametalurgiayi Institute", Armenia*

The present paper endeavors to define operating parameters of the atomic absorption method of spectroscopy for quantitative determination of Chromium in crome ores, crome concentrates and tailings. A new method of preparing standard solutions (in combination with microwave acid digestion of standard samples) is proposed for designing calibration curves and explicating conditions of supplying acetylene gas mixture and nitrous oxide, which enhance the accuracy of results obtained from the quantitative determination of chromium.

Keywords: Crome ore, microwave, standard solution, acetylene gas mixture.

Introduction. Quantitative determination of Chromium in crome ores, crome concentrates and tailings can be performed in compliance with a number of methods [1–5], the most widely accepted of which is the titrimetric method [1, 2]. The method is based on the oxidation of Chromium(III) in sulfuric acid medium over Ammonium persulfate in the presence of catalyst: silver nitrate or mixture of cobalt sulfate and nickel sulfate. Cr(VI) is reduced with Mohr's salt solution, whereas its excess is titrated with potassium permanganate.

Potentiometric and amperometric methods [3, 4], as well as the method of atomic emission spectrometry with inductively coupled plasma (AES ICP) [5], are also widely used for quantitative determination of Chromium in crome ores, crome concentrates and tailings. All the aforementioned methods have a lot of disadvantages: they are quite laborious, requiring application of a number of reagents and long duration of the process. In certain cases it is necessary to neutralize the influence of interfering elements diluting the solution up to certain concentration. Therefore, the entire process becomes more complicated and prolonged, increasing the probability of errors.

We have developed a new method that combines microwave treatment of crome ore with an atomic absorption determination of Chromium. Moreover, the

---

* E-mail: alla-man@mail.ru   ** E-mail: romik@ysu.am

method is bereft of the aforementioned disadvantages [6]. Throughout the entire process of analysis special importance is paid to sample preparation and determination of the optimum operating conditions for performing the analysis, since the accuracy of determination largely depends on these conditions. The present paper sets forth supply conditions of acetylene gas mixture and nitrous oxide. Moreover, preparation methods of standard solutions are studied to increase chromium determination accuracy.

Materials and Method. Acid digestion of the samples has been performed using microwave (MW) system ETHOS TOUCH CONTROL Microwave Labstation ("Milestone", Italy) with 10 autoclaves (Teflon reaction chambers with internal volume of 100 *mL* and operating pressure of 100 *atm*) [6].

Quantitative analysis has been performed by atomic absorption (AAS) spectrometer Varian AA FS 240 (Australia), running in the flame mode of acetylene–air and acetylene–nitrous oxide mixtures.

Crome ore, crome concentrate and tailing samples from Shorzha ore deposit [7, 8] have been used, the chemical composition of which has been determined in advance by different known methods. Table 1 shows the quantitative content of chemical elements at issue.

Sulfuric acid (GOST-4204-77), perchloric acid (GOST 6552-80), hydrochloric acid (GOST-3118-77), Potassium dichromate (GOST-2652-78), crome bar or wire (99.99 %), crome ore № 166-a, crome concentrate № 90 have been used as reagents.

Table 1

The content of some chemical elements in Shorzha deposit ore

Sample type	Chemical elements content, %						
	Cr	Ni	Fe	Ca	Mg	Al	SiO$_2$
Ore	7.00	0.14	6.30	3.25	14.61	1.05	38.06
Concentrate	28.10	0.092	9.25	0.29	6.22	3.00	28.00
Tailing	1.00	0.18	6.00	2.50	22.18	0.20	38.86

Experimental Part and Results. Up to now there are certain impediments as far as it concerns the Chromium quantitative determination using AAS in crome ores, concentrates and tailings. These impediments are primarily determined by the operating conditions of AAS and standard solution parameters required for calibration curve [9]. When using the standard method of AAS one of the methods obviously assumed that the data obtained are false (Tab. 2) in case of acetylene–air and standard solutions (the latter produced by dissolving chemically pure Potassium dichromate or 99.99 % pure crome wire in hydrochloric acid) are used during the analysis to construct the calibration curve. The research shows that sensitivity mainly depends on the type of fire during quantitative determination of Chromium by AAS. So, the mixture of acetylene–nitrous oxide is preferable. In case of any slight deviation from the specified ratio of components in acetylene–nitrous oxide mixture, sensitivity decreases drastically (see Figure). It is known that during AAS quantitative determination of chemical elements, sometimes in the presence of this or that element sensitivity of the method decreases leading to the increase of data error rate.

T a b l e 2

*Chromium content in crome ores, crome concentrates and tailings determined
by various chemical methods*

Sample type	Crome content, %		
	1	2	3
Tailing	0.62	1.02±0.01	1.00
Ore	3.77	7.03±0.01	7.00
Ore № 166-a	12.89	37.37±0.01	37.41
Concentrate	9.65	28.02±0.01	28.00
Concentrate № 90	14.00	40.44±0.01	40.51

Note: 1 – quantitative determination of Chromium has been conducted with Varian AA FS240 atomic absorption spectrometer, required standard solutions for calibration curve are prepared through dissolving chemically pure Potassium dichromate in hydrochloric acid, whereas mixture of acetylene, air was used for the flame; 2 – quantitative determination of Chromium has been conducted using Varian AA FS240 atomic absorption spectrometer, required standard solutions for developing calibration curve were prepared in compliance with the method above, i.e. gas mixture is acetylene/nitrous oxide=7.9/11.0; 3 – quantitative determination of Chromium has been conducted in accordance with titrimetric method.

The Figure displays the data of the absorption of atomic absorption standard solution of Chromium depending on the flow of acetylene, when constant flow of nitrous oxide is given 11.0 *L/min*. As it is shown on the Figure, the best absorption has been achieved in the case of equal flow ratio of acetylene gas and nitrous oxide 7.9/11.0.

This could possibly be explained by the fact that sufficient temperature is not provided for Chromium atomization at a lower stream of acetylene, whereas at high flow absorption the decline is principally determined by poor transparency of the flame [10].

1–20 *mg/L*;   2–50 *mg/L*;   3–150 *mg/L*
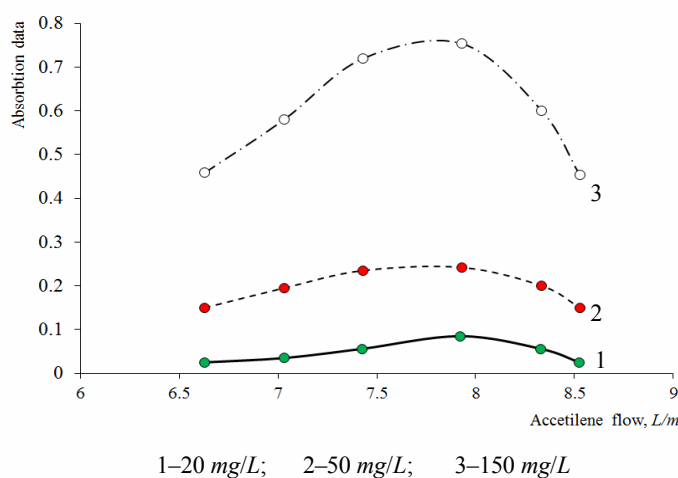
Chromium absorption data from standard solutions based on acetylene flow.
Nitrous oxide flow 11.0 *L/min*, $\lambda = 428.9$ *nm.*

It has empirically been proved that suchlike elements are quite frequent as far as AAS Chromium determination is concerned, however iron and Calcium prevail, which are referred to as attendants in crome ores: iron – 5–15 %, Calcium – 0.3–4.0 % [10].

Two methods of standard solution preparation have been proposed, providing the fact afore, as well as placing special emphasis upon the scientifically substantiated standpoint that the most accurate data have been achieved, when standard solutions for plotting calibration curve are closer to the studied solutions in terms of their chemical composition.

According to the first option, 2.47 *g* of standard chrom concentrate or 2.67 *g* of standard chrom ore samples are needed to obtain a solution with Chromium content of 1.000 *mg*/*mL*. The chemical composition of those samples is provided in Tab. 3.

The standard sample mentioned above was subjected to microwave preparation in compliance with the method proposed by us [6]. Thereafter, the acidic solution acquired was transferred into a measuring flask of 1000 *mL*; the volume was adjusted with distilled water to the mark before being well mixed. The solution thus gained (referred to as "main") can be used for preparing standard solutions with different chromium contents.

In the second option, however, 1.000 *g* of Chromium wire of 99.99 % purity or 2.83 *g* of chemically pure Potassium dichromate was used. Chromium wire was dissolved in hydrochloric acid (25–30 *mL*), whereas Potassium dichromate was dissolved in distilled water.

Table 3

Percentage of chemical elements in standard samples of crome ores and crome concentrates

Sample type	Chemical elements content, %				
	Fe	Al	Cr	Ca	Mg
Ore № 166-a	11.50	5.14	37.41	0.46	8.64
Concentrate № 90	10.98	5.37	40.51	0.19	7.66

Subsequently, the solution has been transferred into a measuring flask of 1000 *mL* adding 5 *mL* of sulfuric acid and 5 *mL* of perchloric acid, as a result of which the volume has been adjusted to 1000 *mL* and well mixed.

The standard solutions thus obtained contain 1 *mg*/*mL* Chromium. Consequently, the so-called "main" solution can be used for preparing standard solutions for calibration curve.

For this purpose, 6 flasks of 100 *mL* were taken and numbered from 1 to 6. 1, 2, 5, 10, 15 and 20 *mL* of the solution, 5 *mL* of a 10% solution of ferric chloride and 1 *mL* of sulfuric acid and perchloric acid have been added in increasing order. The volume of the mixture has been adjusted to 100 *mL* and well mixed.

Operating parameters of atomic absorption have been set forth after preparing standard solutions: 7 *mA* lamp, fuel: acetylene–nitrous oxide, ratio of gas flow 7.9/11.0, wavelength 428.9 *nm*, slit width is 0.5 *nm*, the flame is red and the flattened core height is 1–2 *cm*. The achieved results determine the dependence of the quantity of absorbed chrome upon standard solution concentration, hence, the

calibration curve. Results of the analyses conducted on the basis of proposed standard solutions and already known standard solutions are presented in Tab. 2. It can be clearly stated that the application of standard solutions are suggested in the paper will give more accurate results.

Conclusion. The present paper sets forth quantitative and qualitative ratios of gas mixture required for AAS qualitative determination of Chromium in crome ores, concentrates and tailings. Furthermore, two options of preparing standard solutions are proposed, the application of which enables high level of accuracy of data received from qualitative determination of Chromium (Tab. 2).

REFERENCES

1. **Ponomorev A.I.** Methods for Chemical Analysis of Iron, Titanium Magnetite and Chromium Ores. M.: Nauka, 1966, 405 p. (in Russian).
2. Analysis of Minerals (eds. Yu.N. Knipovich, Yu.V. Morachevkij). L.: GNTKhL, 1959, 1055 p.
3. **Kreshkov A.P.** Course of Analytical Chemistry: Qualitative and Quantitative Analysis. M. Khimia, 1982, 312 p. (in Russian).
4. **Darbinyan H.H., Shaposhnikova G.N., Khachatryan H.G**. The Study of the Interaction of Chromium(VI) with Thiourea by Means of Potentiometry, Spectrophotometry, Amperometry Methods and Its Determination in the Cromium-Containing Ore. // Chemical Journal of Armenia, 2009, v. 62, № 3–4, p. 355–361 (in Russian).
5. **Tormisheva E.A.** PhD. Thesis. Microwave Sample Preparation for Ferroalloys, Magnesia Refractories and Surfacing Powder Analysis by ICP-AES Method. M., 2011, 152 p. (in Russian).
6. Harutyunyan R., Manukyan A., Safaryan A., Gevorgyan A. Chromium Ores Processing Method. Patent AM20120064, 2012-04-23 (in Armenian).
7. **Aloyan P.G., Aloyan G.P., Davtyan A.A., Markosian A.A., Harutyunyan T.M., Stepanyan I.G.** Metals: Ferrous, Nonferrous, Noble Metals, Rare Metals and Rare-Earth (Guide). Yer.: GEOID, 2006, 250 p. (in Russian).
8. J-SC "Lernametalurgiaji Institut" Report for Scientific Research (Grant № 081005 HL). Development of Technology for Concentration of Chromite Ore Deposits Shorzha with the Issuance of Technological Rules for Designing Factory. Yerevan, 2008, 28 p.
9. **Khavesov I., Tsalev D.** Atomic Absorption Analysis. L.: Khimia, 1983, 144 p. (in Russian).
10. **Pupishev A.A.** Atomic Absorption Spectral Analysis. M.: Khimia, 2009, 784 p. (in Russian).