

The Study of Interference Effects and their Elimination in the Determination of Chromium by Flame AAS*

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The extractable content of chromium in various types of soils and sludges from city water treatment using aqua regia and $2 \text{ mol dm}^{-3} \text{ HNO}_3$ was determined. The study of the interferences of Ca, Mg, Fe, Mn, Co, and Ni in the chromium determination in these matrices and the effect of releasing agents NH_4Cl , Na_2SO_4 , $\text{La}(\text{NO}_3)_3$, 8-hydroxyquinoline in the presence of the studied cations was performed. From all the compounds tested as releasing agents in air—acetylene flame, the $10 \text{ g dm}^{-3} \text{ NH}_4\text{Cl}$, 10 g dm^{-3} 8-hydroxyquinoline, and $10 \text{ g dm}^{-3} \text{ Na}_2\text{SO}_4$ gave the best results.

During the last few years chromium determination in environmental and biological samples has received considerable attention owing to its importance not only as an essential element in living organisms but also to its toxicity even at low concentrations [1]. A considerable number of pollution sources are responsible for the presence, accumulation, and mobility of this element in the different environmental compartments. The determination of chromium in an extractable portion of chromium in soil and sludge samples by $2 \text{ mol dm}^{-3} \text{ HNO}_3$ [2] and aqua regia (ISO 11466) [3] is considered to be an important tool for internal control. The substances described in literature [4] as interferents in flame atomic absorption spectrometry are cationic, anionic or acidic matrices resulting from the sample pretreatment and the concomitant species. The interfering cations considered to have significant effect on the chromium determination are Ca, Mg, Fe, Mn, Co, Ni. For air—acetylene flame the main releasing agents found in the literature were NH_4Cl , Na_2SO_4 , $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, 8-hydroxyquinoline, K_2SO_8 .

In this paper the reliable chromium determination in the aqua regia and $2 \text{ mol dm}^{-3} \text{ HNO}_3$ extracts of soil and sludge samples is described. The releasing agents described in the literature were examined to avoid the matrix interferences of the cations, which are the major components of the soil and slightly or severely interfered in the air—acetylene flame. The concentrations of the studied cations were such as determined in soil and sludge extracts.

EXPERIMENTAL

Standard stock solution of 1000 mg dm^{-3} chromium was obtained from Merck (Germany). Working standard solutions were prepared by immediate serial dilution with 1 vol. % nitric acid solution.

The reagents used for the preparation of the releasing agents: NH_4Cl , Na_2SO_4 , $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, 8-hydroxyquinoline, K_2SO_8 were of anal. grade (Lacma, Czech Republic). The concentrated acids (HNO_3 , HCl) were of anal. grade (Merck, Germany).

All solutions were prepared using double deionized water (Labconco, Kansas City, USA).

Reference materials of soil, S-SP (Soil Reference), S-MS (Soil Orthic Luvisols), S-VM (Soil Reference Cambisol), and sludges from city water treatment, WT-L; WT-M; WT-H, were used in this study, produced by the Institute of Radioecology and Applied Nuclear Technique, Košice, Slovak Republic.

Extraction of soil and sludge samples by using $2 \text{ mol dm}^{-3} \text{ HNO}_3$ and aqua regia followed the procedures recommended in [2] and ISO/DIS 11466 [3], respectively.

The determination of chromium was made by employing Perkin—Elmer Model 1100B atomic absorption spectrometer. Measurements were performed on analytical line of 357.9 nm at a spectral band width of 0.7 nm , and a fuel-rich air—acetylene flame with gas supply of 5 and $2.5 \text{ dm}^3 \text{ min}^{-1}$, respectively. No deuterium lamp correction was used.

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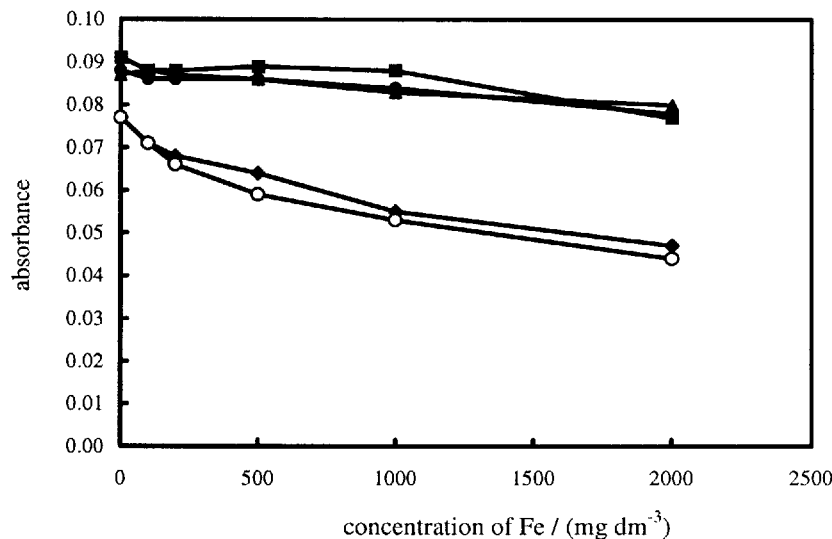


Fig. 1. Effect of releasing agents in the presence of various concentration of Fe on Cr (4 mg dm^{-3}). \blacklozenge Cr (4 mg dm^{-3}) + Fe; \blacktriangle Cr (4 mg dm^{-3}) + Fe + 10 g dm^{-3} oxine; \circ Cr (4 mg dm^{-3}) + Fe + 10 g dm^{-3} La_2O_3 ; \blacksquare Cr (4 mg dm^{-3}) + Fe + 10 g dm^{-3} NH_4Cl ; \bullet Cr (4 mg dm^{-3}) + Fe + 10 g dm^{-3} Na_2SO_4 .

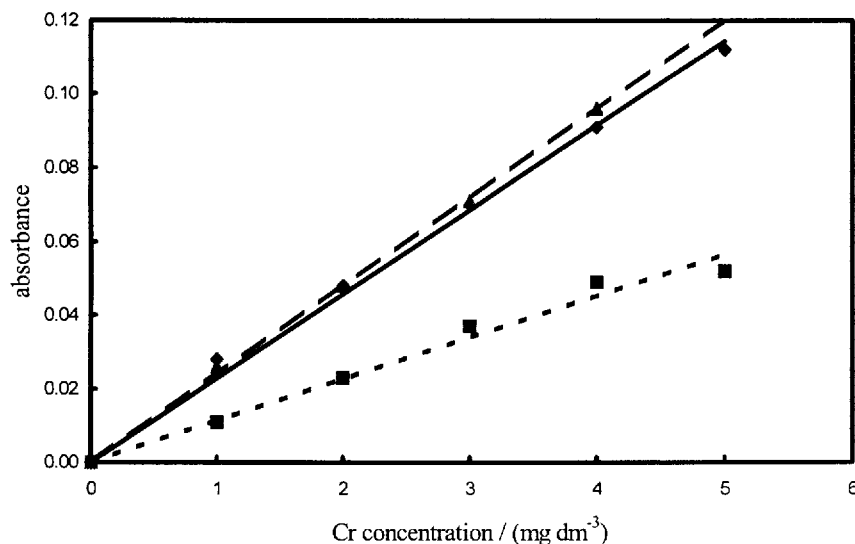


Fig. 2. Effect of the concentration 10 g dm^{-3} of NH_4Cl in the determination of chromium in the presence of Fe ($2000 \mu\text{g cm}^{-3}$). \blacklozenge Cr; \blacksquare Cr + Fe (2000 mg dm^{-3}); \blacktriangle Cr + Fe (2000 mg dm^{-3}) + 10 g dm^{-3} NH_4Cl .

RESULTS AND DISCUSSION

The main problem with respect to the determination of chromium is the effect of the interferences. All the efforts described are focused on the minimization of these effects by using different types of flames as well as by the addition of different releasing or masking agents. The present study was carried out with soil and sludge extracts using 2 mol dm^{-3} HNO_3 and aqua regia solutions for extraction procedures. The interference effect was studied in various chromium/interferent ratios (4 mg dm^{-3} of Cr: Ca/(mg dm^{-3}) 100, 200, 500, 1000, 2000, 4000, 6000; Mg/(mg dm^{-3}) 50, 100, 200, 500, 1000, 1500; Fe/(mg

dm^{-3}) 100, 200, 500, 1000, 2000; Co, Ni, Mn/(mg dm^{-3}) 10, 20, 50, 100, 200, respectively). The maximum concentrations of the cations were as they were determined in these extraction solutions. In the air—acetylene flame the interfering effects were observed by Ca, Mg, Fe, Mn, very severe effect was observed by Fe. No interfering effects were observed for Co and Ni. 10 g dm^{-3} solutions of NH_4Cl , Na_2SO_4 , $\text{La}(\text{NO}_3)_3$, 8-hydroxyquinoline were assayed for the cations which affected Cr determination.

An example of the effect of the releasing agents is presented in Fig. 1 for interference of Fe in determination of 4 mg dm^{-3} of Cr. NH_4Cl , 8-hydroxyquinoline (oxine), and Na_2SO_4 reduced significantly the inter-

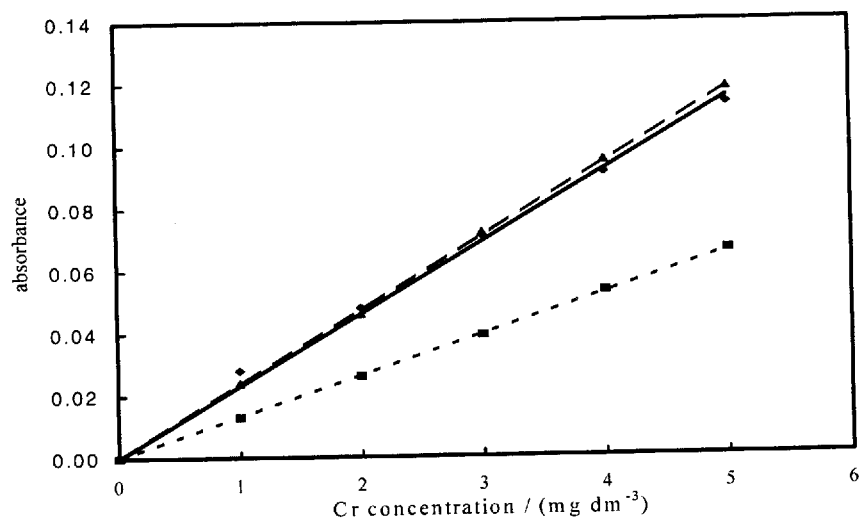


Fig. 3. Effect of the 10 g dm^{-3} of oxine in the determination of chromium in the presence of Fe ($2000 \mu\text{g cm}^{-3}$). \blacklozenge Cr; \blacksquare Fe (2000 mg dm^{-3}); \blacktriangle Cr + Fe (2000 mg dm^{-3}) + 10 g dm^{-3} oxine.

Table 1. Determined Contents of Chromium ($x/(\mu\text{g g}^{-1})$) in Aqua Regia and 2 mol dm^{-3} Nitric Acid Extracts of Soils

Sample	C.V.* (95 % conf. int.)	Aqua regia extracts		$2 \text{ mol dm}^{-3} \text{ HNO}_3$ extracts	
		$\bar{x} \pm \text{SD}$	RSD/%	$\bar{x} \pm \text{SD}$	RSD/%
S-SP	75.3 (72.1—78.4)	28.4 ± 2.2	7.7	6.14 ± 0.85	13.8
S-MS	87.4 (77.0—97.7)	29.6 ± 2.4	8.1	5.56 ± 0.62	11.2
S-VM	79.8 (74.0—85.5)	18.4 ± 1.9	10.3	3.62 ± 0.48	13.3

*Certified values.

Table 2. Determined Contents of Chromium ($x/(\mu\text{g g}^{-1})$) in Aqua Regia and 2 mol dm^{-3} Nitric Acid Extracts of Sludges

Sample	C.V.* $\pm \text{SD}$	Aqua regia extracts		$2 \text{ mol dm}^{-3} \text{ HNO}_3$ extracts	
		$\bar{x} \pm \text{SD}$	RSD/%	$\bar{x} \pm \text{SD}$	RSD/%
WT-L	79 ± 8.3	41.6 ± 3.8	9.1	18.9 ± 1.5	7.9
WT-M	939 ± 53	798 ± 86	10.8	784 ± 73	9.3
WT-H	1342 ± 90	1186 ± 102	8.6	1128 ± 89	7.9

*Certified values.

ference of iron. Effects of $10 \text{ g dm}^{-3} \text{ NH}_4\text{Cl}$ and 10 g dm^{-3} oxine in the determination of chromium in the presence of Fe (2000 mg dm^{-3}) are presented in Figs. 2 and 3.

Formation of crystals in $2 \text{ mol dm}^{-3} \text{ HNO}_3$ and aqua regia extracts of real samples was observed when using 8-hydroxyquinoline. For this reason, the use of NH_4Cl is preferred. The proposed procedure was used for analysis of extracts of soil and sludge samples. The results obtained with the addition of $10 \text{ g dm}^{-3} \text{ NH}_4\text{Cl}$ to the calibrants and to the samples are summarized in Tables 1 and 2. Histograms of percentage of extractable chromium related to the total content of chromium in samples are presented in Figs. 4 and 5.

CONCLUSION

The study of the interferences in the chromium determination in the soil and sludge extracts using $2 \text{ mol dm}^{-3} \text{ HNO}_3$ and aqua regia solutions for extraction procedures and the effect of releasing agents in presence of various cations was performed.

From the results obtained in our experimental it can be seen that the Cr determination is affected by the interferences. The use of fuel-rich air—acetylene flame with the addition of releaser agent leads to reliable results. From all the compounds tested as releasing agents in air—acetylene flame, the concentration dm^{-3} of NH_4Cl gave the best results.

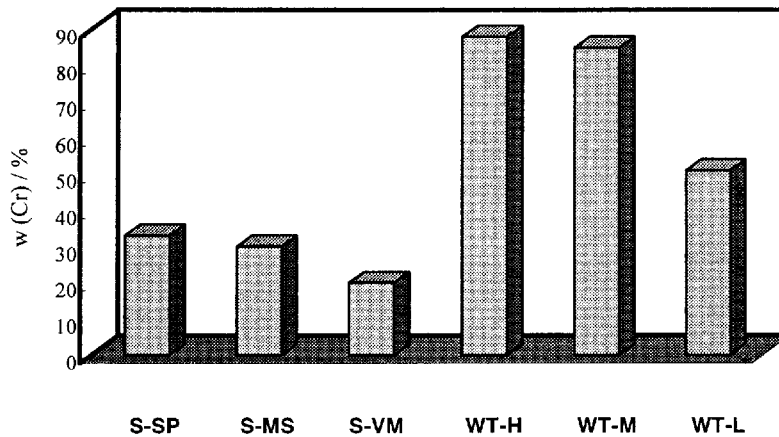


Fig. 4. Cr contents in soil and sludge aqua regia extracts.

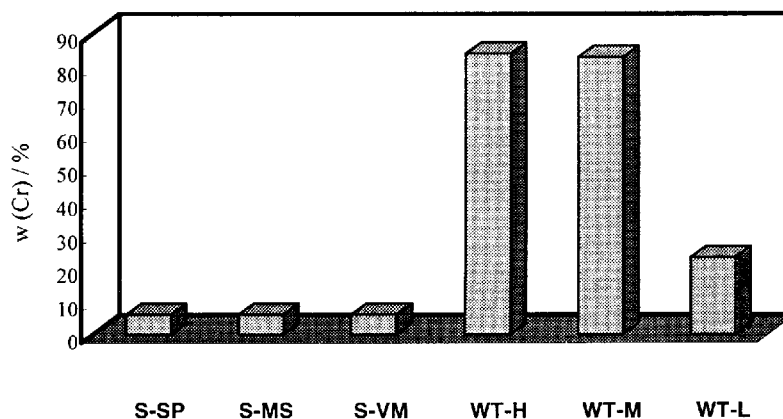


Fig. 5. Cr contents in soil and sludge 2 mol dm⁻³ HNO₃ extracts.

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