DETERMINATION OF CHROMIUM
IN CHLORIDE-CONTAINING MATRIX
USING ET AAS WITH ZEEMAN BACKROUND
CORRECTIONS AND PROGRAMMABLE MAGNETIC
FIELD STRENGTH

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An effective method using the electrothermal atomic absorption spectrometry (ET AAS) with transversally heated graphite atomizer (THGA), Zeeman effect background correction and Rh modifier was proposed for the determination of Cr in chloride matrix. The optimisation of electrothermal program was performed with chromium solution containing 0.5 % (w/v) NaCl and 10 % (v/v) HNO_3 that is a typical matrix of digested instant soups and supplements. The effect of modifier (ascorbic acid, NH_4NO_3, Li, $NH_4H_2PO_4$, Pd, Rh and V) and its concentration on determination of chromium were tested. For each modifier used, a magnetic field strength was also optimised. The significant dependence was

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observed for Pd and especially Rh. In spite of the relatively low concentration of modifiers, a high efficiency of thermal stabilization and excellent sensitivity were obtained for Pd and Rh modifier used (125 mg l⁻¹ Pd and 62.5 mg l⁻¹ of Rh). The characteristic mass was evaluated for NH₄NO₃ 1.7 pg, for V 1.7 pg, Pd 1.0 pg and even Rh 0.9 pg. The methods were recommended for the determination of chromium in digested samples containing high concentration chloride matrix e.g. instant soups and supplements.

Introduction

Chromium(III) is recognised as a trace element that is essential to the human metabolism. Recommended daily intake of chromium is 0.0064 mg kg^{-1} of body weight and day [1]. Technology used in food and beverage processing can increase the natural levels of Cr in raw products. Cr is widely used in the food industry, especially in stainless steel. Monitoring of chromium in fluid/food intake is very important. A decree of the Czech Ministry of Health specifies the maximal allowable content of chromium in foodstuff as 0.2 mg kg^{-1} [2]. Determination of Cr is a challenge to nutrition analyst because of its normally low levels in most food.

Several analytical techniques have been proposed for the determination of Cr in food [1], but graphite furnace atomic absorption spectrometry (ET AAS) has become one of the most popular and most widely used techniques in quality control of food and beverages [3]. ET AAS is a very sensitive analytical technique and requires a low sample volume. In complex sample matrix, problems of spectral interferences such as non-specific background absorption caused by high concentrations of halides and inorganic acids in the sample can occurr. In ET AAS, depression of analyte signals by chloride matrices has been observed and studied for various kinds of samples. Interference could be partly attributed to the physical occlusion of the analyte in the matrix, a gas-phase reaction and/or expulsion. Interference from different kind of chloride e.g. $CaCl_2$, $MgCl_2$, NaCl was reported [5–8].

Routinely applied in ET AAS, the use of chemical modifiers is common to overcome the interference effects. Chemical modifiers are used in order to increase pre-treatment temperature, reduce or eliminate analyte losses and vapour phase interferences and minimise background signals. Some chemical modifiers can increase volatility of unwanted concomitants that are driven off before atomisation of analyte. Tsalev *et al.* [9] published the classification of modifiers, comparison of several modifiers and synergetic effects of mixed modifiers. For elimination of chloride interferences, Slavin *et al.* [10] recommended to use high concentrated HNO_3 or H_2SO_4. López-García *et al.* [5] reported that the presence of HF decreases the background signal caused by NaCl that is supported by the presence of small

amount of HNO_3 without damage to quartz windows and material of the atomiser. Welz et al. [11] described elimination of chloride interferences using Pd modifier with simultaneous addition of hydrogen to the purge gas (5 % H_2/Ar). In this case, Pd is reduced to a different physical form by H_2 and H_2 also reacts with the chlorine forming volatile HCl. Organic compounds with metal matrix modifier show a similar effect [6,12–15]. Platinum group metal (PGM) modifiers (Ir, Pd, Pt, Rh, Ru) are popular metal matrix modifiers at present [15–22]. They have great analytical properties in corrosive chloride matrix as aqua regia [18,19]. In the case of Cr, the effect of Ir, Ru, Zr or Ir + Rh permanent modifier was studied in human serum [20]. Ru permanent modifier was also used for determination of Cr in urine [21]. The pre-treatment temperature was 1400 °C in this case. The high pre-treatment temperatures 1500 °C (Mg, Pd, Pd + Mg) and 1600 °C (Rh, Rh + Mg) were used in the simultaneous determination of Cr and Mn in urine [22]. Tsalev et al. [23] explored V (as NH_4VO_3) as a potential chemical modifier for 25 elements. In the case of Cr, the pre-treatment temperature 1000 °C was obtained. Cabon et al. [14] published pre-treatment temperature 1600 °C for Cr in sea water (S = 1.75 ‰) and 1300 °C in 0.025 mol l^{-1} NaCl solution. Bermejo-Barrera et al. [24] also analysed Cr in seawater. The matrix interferences were completely removed using the high temperature 1600 °C. The detection limit for Cr in seawater was reduced to 0.05 µg l^{-1} using multi-injection technique (100 µl), the Zeeman effect background correction and chemical modification with $CaCl_2$.

With respect to the Czech legally allowable maximal content of contaminants in foodstuff and low Cr content in food, the aim of presented work was to propose a method suitable for the Cr determination in high saline food products (instant soups and spice supplements). Using ET AAS with Zeeman background correction and optimal magnetic field strength, the investigation of the effect of chemical modifiers (ascorbic acid, NH_4NO_3, Li, $NH_4H_2PO_4$, Pd, Rh, and V) that enable direct Cr determination in samples with high NaCl and HNO_3 matrix (typical mineralised instant soup) was carried out. The information provided by this study will assist oven-ready food producers in reduction of pollution of their final products through a better quality control of raw materials, ingredients, and production lines, and ensure their products to meet the requirements of legislation and consumers demands for quality.

Experimental

Instrumentation

A GBC (Dandenong, Australia) model Avanta ULTRA Z atomic absorption spectrometer with fast longitudinal Zeeman-effect background correction system and fitted with a transversally heated graphite atomizer (THGA), and Cr hollow

cathode lamp (Photron) was used in the study. Magnetic field strength can be varied from 0.6 Tesla to 1.1 Tesla. All the measurements were based on both integrated absorbance and peak height absorbance and performed at 357.9 nm. The lamp current and slit-width settings corresponded to the manufacturer's recommendations (6 mA and 0.5 nm, resp.). Milli-Q plus (MILLIPORE, USA) water system was used for preparing deionized water (18.2 MΩ cm^{-1}). Microwave sample digestions were carried out in a Plazmatronika BSM2 microwave system (Plazmatronika, Poland).

Reagents, Materials and Samples

Samples of instant soups were made by Vitana (Czech Republic) and the spice supplement Podravka was made by Podravka (Czech Republic). Instant soups mutually differ only in flavour and they usually contain basic ingredients as follow: dried vegetables, meal, egg and spices, potato stark, wheat flour, milk proteins, vegetable fat, salt, aromatic ingredients etc. The spice Podravka contains a mix of spice and salt mainly. As producers declare, the NaCl content in dry matter of instant soup varies from 7 % to 13 % w/w and the total dry matter is about 98 %.

All chemical reagents used for measurements were analytical grade: 65 % (w/v) HNO$_3$, 30 % (w/v) H$_2$O$_2$, NH$_4$NO$_3$, NH$_4$H$_2$PO$_4$, ascorbic acid and NaCl (Lachema, Brno, Czech Republic). The Cr and V stock solution 1000 ± 2 μg ml^{-1} was used (Analytika, Praha, Czech Republic). The modifiers used were 1000 ± 3 μg ml^{-1} Pd stock solution (Pd in 4 % v/v HNO$_3$), 1000 ± 3 μg ml^{-1} Rh stock solution (as ((NH$_4$)$_3$RhCl$_6$ in 10 % HCl), both made by SCP Science, Canada. Argon as a shield gas was purity 99.999 %.

Sample Preparation

The instant soup samples were digested in a microwave system with an evaporation step after the digestion: 1 g of homogenized dry matter of instant soup was accurately weighed into an acid washed teflon digestion tube. Nitric acid (12 ml; 65 % w/v) and 1ml H$_2$O$_2$ (30 % w/v) was added, and the tube was heated in a microwave oven at the power setting of 80 % for 10 min and at 100 % for 10 min. The maximum total output of the microwave generator was 700 W (minimum pressure = 24 105 Pa, maximum pressure = 25 105 Pa). A redundant amount of HNO$_3$ was evaporated. After decomposition, the digested sample was diluted with deionised water to the final volume of 25 ml.

On the basis of known digested instant soup matrix, the artificial sample was prepared and used in the study. Declared by producer, the NaCl content in dry

matter of instant soup varies in the range from 7 to 13 % w/w. Considering "dilution of sample" within pre-treatment step, the maximum NaCl content was 0.52 % w/v in the decomposed sample. In order to optimise conditions of measurements, all experiments were made with samples containing 4 μg l^{-1} Cr, 0.5 % (w/v) NaCl and 10 % (v/v) HNO_3, which is a typical matrix of digested instant soups and supplements.

The initial concentration 0.5 g l^{-1} Pd, Rh and V modifiers was used. For NH_4NO_3 or $NH_4H_2PO_4$, the primary concentration was 2 % (w/v) and for ascorbic acid 10 % (w/v).

Procedures

Cr was directly determined by ETA AAS in the artificial Cr sample and mineralised instant soups, under the conditions shown in Table I. In the study, the injection volumes were constant: 30 ml of sample (Cr artificial solution or mineralised sample) and 4 ml of a chemical modifier. The samples were injected on a preheated graphite surface (injection temperature 60 °C). The studied chemical modifiers included ascorbic acid, NH_4NO_3, $NH_4H_2PO_4$, V, Li, Pd and Rh, each used in new atomisers to avoid possible memory effects. The study used the optimal amount of modifier, the thermal program conditions for Cr determination with matrix and the optimal magnetic field strength. For comparison, both integrated absorbance and peak height were measured throughout the study and the signal values are the average of triplicate injections in all the cases. In order to provide the same results of measurements of peak height and integrated peak area, the peak height was preferred in the presented figures due to it quaranteed better sensitivity. In all the tables and figures, the given amounts of analyte, interferent or matrix modifier are those present in the final volume injected into the graphite tube.

Results and Discussion

Matrix effect

All our experiments were carried out with very corrosive matrix containing high concentration of chloride and HNO_3 where volatility of chromium was increased. In Fig. 1, the pyrolysis curve for artificial Cr solution is displayed. Clearly, Cr it is not held in tube and evaporates at low temperature. The non-specific absorption of background is high up to approx. 920 °C, then NaCl starts to vaporise and is not observed at the temperatures above 1200 °C any more. Our observations are in good agreement with the results obtained by Castro *et al.* [23] who measured

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Table I Heating program for determination of Cr in samples containing NaCl

Step	Temperature, °C	RAMP, s	Hold, s	Ar flow*
Drying	110	20	8	on
Drying	150	10	15	on
1st pre-treatment	350	10	5	on
2nd pre-treatment	■	10	15	on
Delay	■	0	0.5	off
Atomisation	2500	▼	2	off
Cleaning	2500	0	2	on

* The Ar flow rate was 3 l min^{-1}
■ The optimized pre-treatment temperature for tested modifiers ranged from 1000 to 1300 °C
▼ The highest RAMP for optimized pre-treatment temperature for tested modifiers was 0.4 – 0.6 s

NaCl retained on the graphite surface by energy disperse X-ray spectrometry. To completely eliminate interferent effect of NaCl on the absorption signal of analyte, the chemical modifier has to stabilize analyte at least up to 1200 °C.

Chemical Modifiers

The use of matrix modifier is always required for the determination of chromium in salt matrices, increasing analyte thermal stability and thus providing higher pyrolysis temperatures for the removal of high contents of concomitants. According to literature search, many chemical modifiers are used for matrix effect removing in Cr determination. In the present work, ascorbic acid and NH_4NO_3 were examined as reagents increasing volatility of unwanted concomitants, Li as reagent reducing vapour phase interferences and modifiers $NH_4H_2PO_4$, Pd, Rh and V in aqueous solution for thermal stabilization of chromium. According to Fig. 1, it is necessary that the chemical modifier ensures the stabilisation of analyte at least up to 1200 °C for satisfactory elimination of non-specific background signal caused by NaCl.
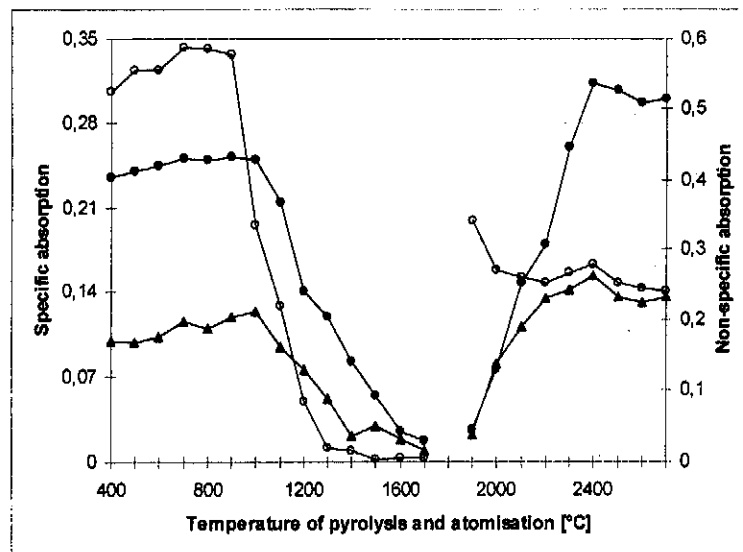
Fig. 1 Pyrolysis "a" and atomization "b" curve for artificial Cr solution (0.5 % (w/v) NaCl and 10 % (v/v) HNO₃). No modifier was used. The temperature of atomization for the pyrolysis curve was set at 2500 °C. The temperature of pyrolysis for the atomization curve was set at 1000 °C. Peak area (▲), peak height (●); non-specific absorption of background (○)

Optimising of the Electrothermal Program

The heating program was optimised for each modifier tested. The temperature and time of drying steps were set up visually with assistance of the spectrometer camera. The optimisation of electrothermal programme was done with preliminary concentration: 1 % (w/v) NH_4NO_3, 5 % (w/v) ascorbic acid, Li 125 mg l⁻¹, 1 % (w/v) $NH_4H_2PO_4$, V 125 mg l⁻¹, Pd 125 mg l⁻¹ and Rh 62.5 mg l⁻¹, the magnetic field strength 1T and the atomisation temperature 2500 °C. For each modifier tested, the pyrolysis curve and the non-specified signal of background for the pyrolysis curve are displayed in Fig. 2.

Using commonly recommended NH_4NO_3 modifier [24], the background absorption decreased satisfactorily but Cr remained in the tube without any loss only up to the pre-treatment temperature 1000 °C. A high injected amount of NH_4NO_3 caused fast contamination of the quarz window of the atomizer head. In the case of ascorbic acid, absorption of background was really decreased together with specific absorption of Cr that was slowly decreased from 800 °C unfortunately. Ascorbic acid alone was not used for other experiments. Li and $NH_4H_2PO_4$ also did not provide satisfactory results. $NH_4H_2PO_4$ produces higher background absorption and does not stabilise Cr to high pre-treatment temperature
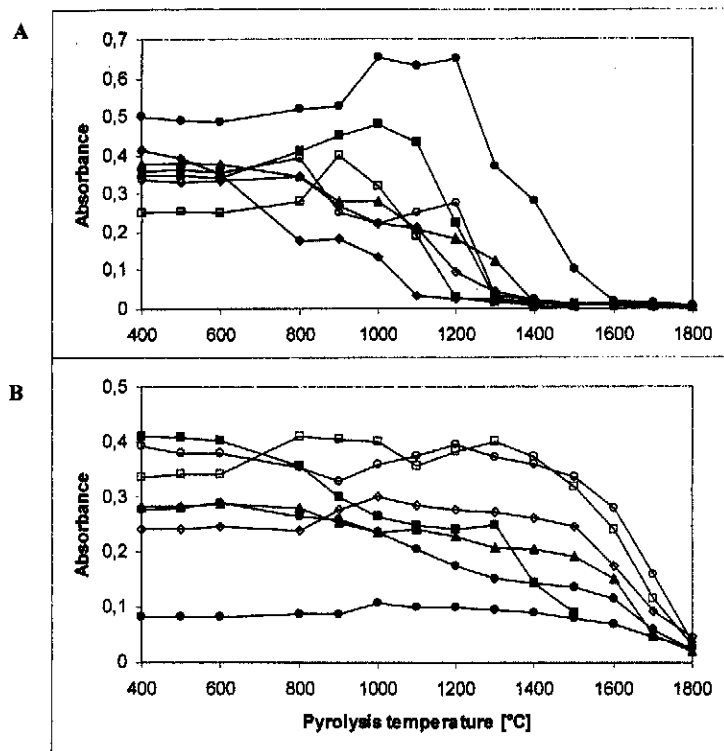
Fig. 2 Pyrolysis curve for Cr in 0.5 % (w/v) NaCl and 10 % (v/v) HNO_3 for the modifier used: A – non-specific absorption signal (backround) for modifier; ascorbic acid (■), Li (▲), NH_4NO_3 (◆), $NH_4H_2PO_4$ (●), Rh (□), Pd (○), V(◇); B – specific absorption (peak height) for the same modifiers

Table II   Results and sensitivity characteristics for determination of Cr in artificial solution containing 0.5 % (w/v) NaCl and 10 % (v/v) HNO_3

Modifier	T_{pyr} °C	c mg l^{-1}	MF T	m_H pg	m_A pg	D_{LH} pg	D_{LA} pg
NH_4NO_3	1000	10000	0.8	1.68	6.06	0.055	0.18
V	1050	250	1	1.38	4.43	0.041	0.16
Pd	1200	125	1	1.06	4.43	0.031	0.15
Rh	1300	32.5	0.95	0.89	3.61	0.027	0.12

T_{pyr} – pre-treatment temperature; c – modifier concentration; MF – magnetic field; m_H, m_A – characteristic mass calculated from peak height or peak area; D_{LH}, D_{LA} – detection limit calculated from peak height or peak area

and the chloride matrix could not be eliminated. We found that modifiers containing Pd, Rh and V keep Cr in a tube at temperatures above 1000 °C. These modifiers and NH_4NO_3 were used for the following experiments. The optimised pre-treatment temperatures for Cr were 1000 °C for NH_4NO_3 (preliminary concentration 1 % w/v), 1050 °C for V (initial concentration 125 mg l^{-1}), 1200 °C for Pd (125 mg l^{-1}) and 1300 °C for Rh (62.5 mg l^{-1}). In case of Rh modifier that allows using the pre-treatment temperature 1300 °C, background absorption was completely eliminated. For the chosen modifiers used, the pre-treatment temperatures for Cr are summarised in Table II.

Optimisation of the Chemical Modifier Concentration

In the second step, the concentrations of selected chemical modifiers (NH_4NO_3, Pd, Rh and V) were optimised. The optimisation of modifier concentration was based on geometric series: the initial concentration of modifier was diluted gradually 2×, 4×, 8×, 16×, 32× etc. The optimised modifier concentrations are displayed in Table II. In order to make V chemical modifier effective and able to stabilise chromium at high temperatures, a large amount of modifier is needed (2000 ng). In the case of Pd modifier, it was recorded that sensitivity was improved up to amount of 500 ng Pd in a tube. Higher amounts of Pd modifier *vice versa* reduced the signal of chromium (Fig. 3). Rh modifier seemed to be very effective (see Fig. 2). In connection with increasing amount of Rh in the atomiser, a higher specific absorbance of Cr was found together with growing RSD. For that reason, the injected amount 250 ng of Rh was chosen for other experiments. Oliveira *et al.*described a similar observation in the case of determination of manganese in urine [22]. They assumed that using of more concentrated Rh solutions makes the surface permanently modified and an analyte is occluded.

Optimisation of the Magnetic Field Strength

The AA spectrometer that was used in this work allows changing the magnetic field strength from 0.6 T to 1.1 T. The effect of a magnetic field strength on sensitivity is described very rarely [25–29]. The magnetic field strength was optimised for each modifier tested. We found out that determination of chromium with various chemical modifiers used requires a different value of magnetic field. For different modifiers, the dependences of absorbance on increasing magnetic field strength are shown in Figs 3 and 4 for chromium in chloride matrix. The pictures show that the better thermally stabilized alloy "Chromium-modifier" has the stronger dependence on magnetic field.
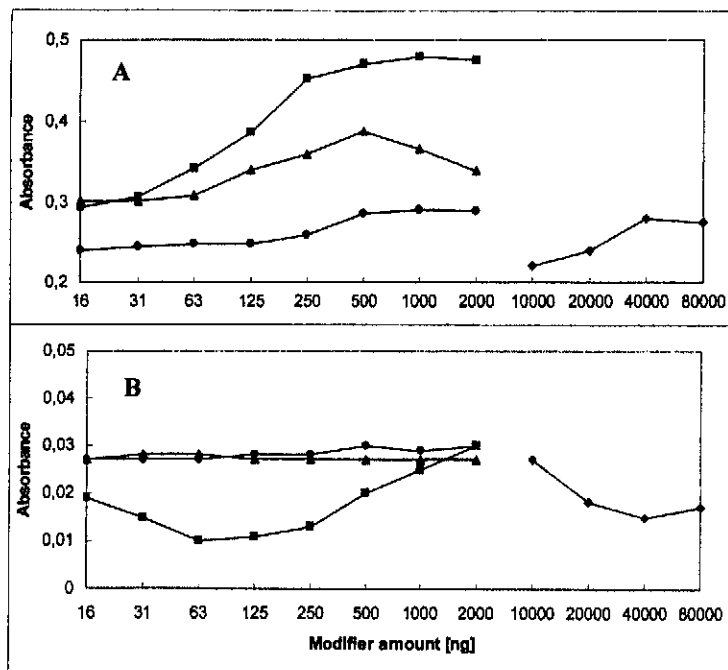
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Fig. 3 Effect of increasing modifier amount (4 µl injected) on the peak height absorbance and non-specific absorption of backround in 0.12 ng Cr determination: A – Specific absorption (peak height) for modifier Rh (■), Pd (▲), V(●), NH_4NO_3 (◆); B – non specific absorption (backround) for the same modifiers
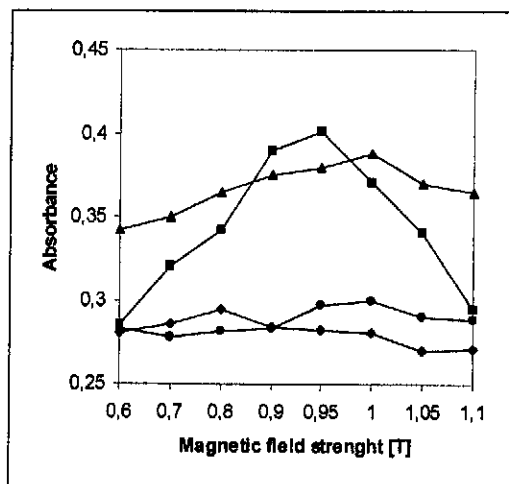

Fig. 4 Effect of magnetic field strength on integrated absorbance of 0.12 ng Cr in 0.5 % (w/v) NaCl and 10 % (v/v) HNO_3 for: 0.25 µg Rh (■), 0.5 µg Pd (▲),1 µg V(●), 400 µg NH_4NO_3 (◆)
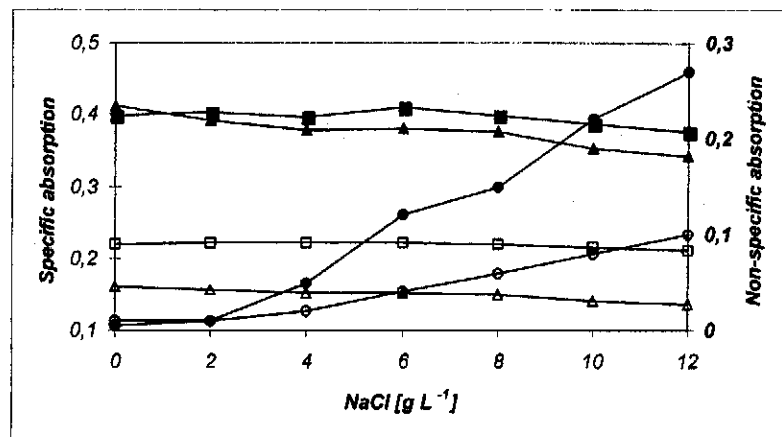
Fig. 5 The interference curve for NaCl in 10 % (v/v) HNO$_3$. Determination of 120 pg Cr with 0.5 μg Pd modifier (T_P = 1200 °C, T_A = 2500 °C, *IMP* = 1T, t_p = 60 s). Determination of 120 pg Cr with 0.25 μg Rh modifier (T_P = 1300 °C, T_A = 2500 °C, *IMP* = 0.95T, t_p = 60 s). Pd modifier: (▲) specific absorption of Cr-peak height, (△) Cr-peak area, (●) non-specific absorption of background; Rh modifier: (■) specific absorption of Cr-peak height, (□) Cr-peak area, (○) non-specific absorption of background

Optimised Analytical Method

By using the optimised heating program, modifier concentration and magnetic field strength, the excellent sensitivity and low characteristic mass values for chromium were obtained (Table II). In relation to better sensitivities for Pd and Rh modifiers used, these ones were employed in the "robustness" study and for instant soup samples analysis.

Matrix Modifier Robustness

Under optimised analytical conditions and with respect to unknown and varying concentration of NaCl in instant soups, the ability of modifiers Pd and Rh to remove matrix effect was tested for 0 to 12 g l^{-1} NaCl in artificial samples containing 10 % (v/v) HNO$_3$. From interference curves, decrease of the specific absorbance of Cr was apparent from 10 g l^{-1} NaCl in sample. This decrease is more significant for Pd than Rh modifier and probably coheres with lower temperature of pyrolysis used for Pd. Below this temperature, less NaCl amount is evaporated and higher chloride concentration remains in the atomiser than in the presence of Pd modifiers and the non-specific absorption of background increases (Fig. 5).

Analytical Characteristics

By using Cr reference solutions and the optimal thermal conditions established for Cr with Pd and Rh modifiers, we obtained linear calibration curves in the calibration range $0 - 5$ μg l^{-1} for both Pd and Rh modifiers. For comparison, both peak height and peak area evaluation of specific absorbance is presented. Better detection limits and characteristic mass and higher calibration slopes were reached in the case of the peak height (Table III).

Table III Calibration characteristics for Cr in 0.5 % (w/v) NaCl and 10 % (v/v) HNO_3

Modifier	Pd		Rh	
	Peak height	Peak area	Peak height	Peak area
Calibration range	$0 - 5$ μg l^{-1}			
Slope ±SD	0.0954 ±0.000672	0.0373 ±0.000423	0.104 ±0.000800	0.05252 ±0.000417
Intercept ±SD	−0.000448[a] ±0.0020	−0.000943[a] ±0.0128	0.0259[a] ±0.0242	0.00180[a] ±0.00126
Correlation coefficient	0.9965	0.9991	0.9996	0.9996

[a] The intercept found is statistically insignificant

Table IV Results of determination of Cr in instant soups using the optimised ET AAS method (0.25 μg Rh modifier, T_P = 1300 °C, T_A = 2500 °C, *IMP* = 0.5 T, t_p = 60 s)

Instant soup	Cr[a] μg kg^{-1}
Fish soup	210 ± 5.7
Pea soup	160 ± 4.1
Tomato soup	73 ± 2.1
Spring soup	20 ± 0.6
Spice mixture Podravka	1150 ± 17.1

[a] mean ± standard deviation

Analysis of Soup Samples

The methodology (0.25 μg Rh modifier; T_P = 1300 °C, T_A = 2500 °C, *IMP* = 0.95T, t_p = 60 s) was applied to the mineralised instant soups. In analysed samples, Cr was found in wide concentration range from 20 μg kg^{-1} Cr for the

Spring soup up to 1150 $\mu g\ kg^{-1}$ Cr for the spice mixture Podravka (Table IV). Due to the fact that no certified reference materials are available, the procedure was validated using the standard addition method. The results obtained from the direct determination using the linear calibration model were compared with analysis of the standard addition technique. The differences between the results of both procedures were statistically insignificant.

Conclusion

For the determination of chromium in salt matrices, the matrix modifiers ascorbic acid, NH_4NO_3, Li, $NH_4H_2PO_4$, Pd, Rh and V were tested. For constant magnetic field strength 1 T, the optimisation of electrothermal programme was done for each chemical modifier. The commonly recommended NH_4NO_3 modifier ensured satisfactory removing of matrix and decreasing of the background absorption but Cr was held in a tube only up to 1000 °C. In case of ascorbic acid, the non-specific absorption decreased together with specific absorption of Cr from 800 °C. Li and $NH_4H_2PO_4$ also did not provide satisfactory results. Pd, Rh and V held Cr in a tube at temperatures above 1000 °C. The optimised pre-treatment temperatures were 1050 °C for V and 1200 °C for Pd. In the case of Rh modifier that allows using the pre-treatment temperature of 1300 °C, background absorption was completely eliminated.

For modifiers suitable from the point of view of convenient temperature of pyrolysis, the concentrations were optimised. In the case of V modifier, the sensitivity increased up to injected 2000 ng, for Pd up to amount 500 ng and then the decrease in the specific absorption of chromium was noticed. In connection with increasing amount of Rh in the atomiser, a growing specific absorbtion of Cr was found up to 500 ng together with growing RSD. The injected amount 250 ng Rh was established. Only Pd and Rh modifiers ensured excellent sensitivity. The magnetic field strength was optimised for these modifiers. The determination of Cr with various chemical modifiers used requires an optimised value of magnetic field due to that the dependences of absorbance on magnetic field strength are specific not only for various elements analysed but also for the modifier used.

Due to the fact that the spectrometer that was employed in this study allows really very fast and uniform heating of THGA, the atomisation temperature can be reached in a very short time. On that account, the sensitivity (characteristic mass) is approximately 3 – 4 times better for peak height absorbance than integrated absorbance calculated from peak area.

The Rh modifier gives the best analytical characteristics from all the tested chemical modifiers (the highest pre-treatment temperature, the best sensitivity, low modifier concentration used and the longest tube lifetime). For the Rh modifier, the chromium characteristic mass calculated from peak height was evaluated to

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excellent 0.89 pg and the characteristic mass from peak area 3.61 pg. These characteristic masses are lower then the values published for determination of Cr in samples containing chlorides, e.g. urine [19,20]. Chromium was determined in different types of instant soups and supplements. The influence of real samples matrix (concentration of NaCl in digested samples was not higher than 0.52 % w/v) was tested. The method of standard additions was used for four different types of instant soups and one spice mixture. The recoveries for Rh modifier were between 96 and 103 % in all the cases, and the influence of matrix was very well eliminated using Rh modifier, high pre-treatment temperature and optimised magnetic field. The Cr amount in real samples was evaluated from linear calibration model. In digested instant soups and supplements, the Cr amounts were found between 0.8 μg l^{-1} and 46 μg l^{-1}. In dry basis, the real content of Cr was between 20 and 1150 μg kg^{-1}. For determination of chromium in digested samples containing high chloride concentration e.g. instant soups and supplements, the method using Rh modifier can be recommended.

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