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ORIGINAL PAPER

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Multielement electrothermal atomic absorption spectrometry: A study on direct and simultaneous determination of chromium and manganese in urine

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Abstract A study was carried out on the direct determination of Cr and Mn in urine using simultaneous atomic absorption spectrometry (SIMAAS). The heating program conditions, the absorbance signal profiles, the influence of different chemical modifiers, and the urine sample volume delivery into the tube were optimized to perform the calibration with aqueous solutions. Among several chemical modifiers tested, the best recovery and repeatability results were obtained for 3 μg $Mg(NO_3)_2$. On using this modifier, the pyrolysis and atomization temperatures for simultaneous determination of Cr and Mn were 1300 °C and 2500 °C, respectively. Urine samples were diluted (1+1) with 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100 prepared in high purity water. A 20-μL aliquot of analytical solution and 10 μL of chemical modifier solution were delivered to the graphite tube. The characteristic masses were 7.8 pg for Cr (RSD=4.0%) and 4.6 pg for Mn (RSD=2.6%). The limits of detection were 0.08 μg L^{-1} (n=20, 3*s*) for Cr and 0.16 μg L^{-1} (n=20, 3*s*) for Mn. Recovery studies for 1.0 or 2.5 μg L^{-1} of Cr and Mn added to different urine samples showed acceptable results for Cr (100%, RSD=14%) and Mn (88%, RSD=5.6%).

Introduction

Chromium and manganese are essential elements for humans. Chromium is required for the maintenance of normal glucose, cholesterol, and fatty acid metabolism and also as cofactor in the initiation of peripheral insulin action [1, 2]. Manganese plays an important role in bone and tissue formation, reproductive functions, and carbohydrate and lipid metabolism [2]. However, abnormal concentrations of chromium and manganese in humans can have detrimental effects on health, e.g., cancer and Parkinson's disease, respectively [2, 3, 4].

Absorption via inhalation, ingestion, and skin contact are the main routes of contamination during occupational exposure [1]. Therefore, it is very important to perform regular monitoring of chromium and manganese levels in endangered populations to minimize health risks arising from environmental and occupational exposure.

Urine is one of the main routes of excretion and can be used for toxicological and therapeutic investigations [1]. The concentrations of many elements of interest in urine are at trace or ultra-trace levels, e.g., chromium and manganese concentrations of approximately 1.0 μg L^{-1} are reported in the urine of healthy people [1, 5]. Due to this low concentration, the determination of chromium and manganese has to be carried out with high-sensitivity methods [5, 6].

Graphite furnace atomic absorption spectrometry (GFAAS) offers a combination of attractive characteristics facilitating such determinations: it is one of the most sensitive and selective spectroscopic techniques; it requires a low sample volume; and it frequently has no need of laborious sample pretreatment –the sample is merely diluted and introduced directly into the graphite tube. Because of these characteristics, GFAAS has been successfully used for the determination of trace and ultra-trace elements in biological fluids [5], e.g., chromium [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17] and manganese [18, 19] in urine.

Simultaneous atomic absorption spectrometry (SIMAAS) has overcome the main drawback of ETAAS – up to six elements can be detected after only one heating cycle [20, 21, 22], reducing analytical time and costs associated with replacement of the graphite components. Like any other multielement technique, SIMAAS requires that certain compromises are made regarding the operating conditions, e.g., pyrolysis and atomization temperatures and chemical modifier, which can lead to a significant loss of sensitivity [5]. The use of the transversely heated graphite atomizer with integrated platform and Zeeman-effect background correction under STPF conditions helped to overcome these adversities, allowing more flexible com-

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promises. Development of methods for the two-element operating mode reduced the instrument operation time sample and reagent consumption.

Simultaneous multielement spectrometers have been used in clinical analysis of cadmium and lead in whole blood [23], copper, iron, and zinc [24] and aluminum, cobalt, chromium, manganese, molybdenum, nickel, and vanadium [25] in serum, and cobalt and manganese in urine [26].

In this work the simultaneous determination of chromium and manganese in urine using a transversely heated graphite atomizer with integrated platform, Zeeman-effect background correction, Echelle polychromator, and hollow cathode lamps as light sources was investigated.

Experimental

Instrumentation

A simultaneous atomic absorption spectrometer, SIMAA-6000 (Perkin-Elmer, Norwalk, CT, USA) equipped with a pyrolytically coated THGA tube with integrated platform (Part Number B3 000641), Zeeman-effect background correction system, Echelle polychromator, and hollow cathode lamps from Perkin-Elmer, was used for simultaneous two-element determination. The analytical reference, sample, and the chemical modifier solutions were taken from polypropylene cups and delivered to the graphite tube by means of an AS-72 autosampler. The equipment was controlled by AA Winlab™ software version 2.5 (Perkin-Elmer, Norwalk, CT, USA).

Argon 99.999% (v/v) (Air Liquide Brasil S/A, São Paulo, SP, Brazil) was used as purge gas.

Reagents

All chemicals used were of analytical reagent grade (Merck, Darmstadt, Germany). The analytical reference and sample solutions were prepared using high purity deionized water obtained by a Milli-Q® water purification system (Millipore, Bedford, MA, USA). Nitric acid was distilled in quartz sub-boiling stills (Marconi, Piracicaba, SP, Brazil).

The 1000 mg L^{-1} chromium and manganese stock solutions were prepared by dissolving Tritisol Standard in deionized water. Chemical modifiers were prepared by using Suprapur salts $Mg(NO_3)_2$ and $Pd(NO_3)_2$ (Merck, Darmstadt, Germany) and $RhCl_6$ (Aldrich, Milwaukee, WI, USA). Triton X-100 (Merck, Darmstadt, Germany) was used as a surfactant.

Procedure

All glassware and plastic bottles were cleaned by washing with detergent solutions and soaking in 10% (v/v) HNO_3 for 24 h, They were finally rinsed with Milli-Q® water and dried in a polypropylene container. The autosampler cups of the SIMAA-6000 were cleaned with nitric acid vapor inside a microwave vessel [27].

The operating conditions and the heating program employed for optimization of the procedure are shown in Table 1. This study was carried out with a reference solution containing 5.0 μg L^{-1} of chromium and manganese in 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100. This solution was also used to spike chromium and manganese in urine samples for attaining concentrations of 1.0 or 2.5 μg L^{-1}.

The following chemical modifiers were tested: (1) 3 μg $Mg(NO_3)_2$; (2) 10 μg $Mg(NO_3)_2$; (3) 5 μg Pd; (4) 10 μg Pd; (5) 5 μg Pd + 3 μg $Mg(NO_3)_2$; (6) 5 μg Rh; (7) 10 μg Rh; (8) 5 μg Rh + 3 μg $Mg(NO_3)_2$ in 1.0% (v/v) HNO_3. Pyrolysis temperature curves with and without the addition of chemical modifier were recorded for reference and urine (1+1) solutions containing 2.5 μg L^{-1} of chromium and manganese in 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100. The atomization temperature was 2500 °C.

The calibration reference solutions were prepared in the autosampler cups (total volume=1200 μL) by dilution (1+1) of the previously prepared solutions containing 1.0, 2.0, 3.0, 4.0, and 6.0 μg L^{-1} of Cr and Mn in 4.0% (v/v) HNO_3 + 0.10% (w/v) Triton X-100 with high purity water.

The first morning urine was collected from eight male and two female healthy volunteers directly in chromium and manganese free bottles (Nalge Company, Rochester, NY, USA) and were kept in a refrigerator (4 °C). The majority of the volunteers had not been exposed to any sources of chromium and manganese and were between 20–25 years old. Two volunteers, one male and one female aged 49 and 54 years, respectively, were cigarette smokers. Determinations of chromium and manganese were performed up to 24 h after sample collection. The well-mixed and undiluted urine samples were pipetted directly onto the autosampler cups and diluted (1+1) with 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100.

In all experiments, 20 μL of reference or samples solutions and 10 μL of chemical modifier were injected in the pre-heated (100 °C) graphite tube.

All measurements were performed with at least three replicates and based on integrated absorbance.

Table 1 Instrumental operating conditions and THGA heating program for simultaneous determination of chromium and manganese a

	Chromium	Manganese		
Wavelength (nm)	357.9	279.5		
Bandpass (nm)	0.7	0.7		
HCL current (mA)	20	15		
Read delay (s)	1	0		
Read time (s)	6	5		
Measurement mode	Peak area	Peak area		
Heating program				
Step	T (°C) [b]	Ramp (s)	Hold (s)	Ar flow (mL min^{-1})
Drying 1	110	1	20	250
Drying 2	130	5	10	250
Pyrolysis 1	800	5	20	250
Pyrolysis 2	1300	10	15	250
Atomization	2500	0	5	0
Cleaning	2600	1	2	250

[a] Program time: 94 s; cycle time: ca 130 s; injection temperature: 100 °C; pipette speed: 40%
[b] Nominal values

Results and discussion

Simultaneous multielement determination using SIMAAS requires selection of compromise instrumental and chemical conditions for the elements which can lead to the best sensitivity. The need to reach a compromise with regard to conditions for the heating program, e.g., pyrolysis and atomization temperatures, chemical modifiers for multiple analytes, and the limited working range of this technique have to be borne in mind [5, 28]. The pyrolysis temperature is one of the critical parameters for improving the selectivity and reducing vapor phase interference in ETAAS measurements [5]. For complex matrices, e.g. urine, the pyrolysis temperature and hold time should be set giving due consideration to the sample dilution, the chemical modifier, and the thermal stability of the elements to be determined [18].

The thermal characteristics of chromium and manganese, the difference of 100 K between the pyrolysis and 400 K between the atomization temperatures, according to the instrumental settings recommended by the manufacturer, are favorable for simultaneous determination of these elements.

Due the high thermal stability, the determination of chromium in urine has been performed without a chemical modifier [8, 9, 13, 18]. Otherwise, chemical modifiers such as Pd or $Mg(NO_3)_2$ [15, 16, 17] have been successfully employed. Manganese was readily determined by using $Mg(NO_3)_2$ [19, 26] as chemical modifier. Based on this previous work, we investigated several combinations of Pd and $Mg(NO_3)_2$ as chemical modifiers for simultaneous determination of chromium and manganese in urine. Additionally, we also investigated the behavior of Rh and the mixture Rh + $Mg(NO_3)_2$ as chemical modifier. The analytical performance of the chemical modifiers studied was based on the thermal stabilization, characteristic mass, recovery tests, and the outline of the absorbance signal.

The results obtained at various pyrolysis temperatures and the characteristic mass (m_o) values for the simultaneous determination of chromium and manganese are shown in Table 2. All chemical modifiers tested did not cause any appreciable thermal stabilization of chromium and manganese. With 3 μg $Mg(NO_3)_2$ and 10 μg $Mg(NO_3)_2$ as chemical modifiers, the pyrolysis temperatures are in accordance with those reported for monoelement instrument detection [18,20]. However, manganese atomization was strongly affected by 10 μg $Mg(NO_3)_2$; double and triple peaks were observed, showing the interference of very high masses of magnesium nitrate in manganese atomization [29]. 5 or 10 μg of Pd raises the pyrolysis temperature for chromium up to 1500 °C and for manganese up to 1300 °C. For the mixture 5 μg Pd + 3 μg $Mg(NO_3)_2$, the maximum pyrolyis temperatures for chromium and manganese were 1500 °C and 1400 °C, respectively. Use of 5 or 10 μg Rh as modifier raises the pyrolysis temperature for manganese to 1200 °C, while for the mixture 5 μg Rh + 3 μg $Mg(NO_3)_2$ the maximum pyrolysis temperature was 1300 °C. However, when a high concentration of rhodium was used (10 μg Rh) a memory effect was observed for manganese. Probably, after several heating cycles, the integrated platform surface of the THGA tube could be permanently modified with Rh, occluding manganese species which were not complete volatilized during the clean-up step. This hypothesis was confirmed when the blank solution was introduced into the graphite tube after fifteen successive heating cycles of 2.5 μg L^{-1} of chromium and manganese using 10 μg Rh as chemical modifier. In this situation, the high manganese absorbance signals observed for blank solution (A=0.0229±0.001, n=5) diminished to an acceptable level after about 10 heating cycles on using the heating program presented in Table 1.

Table 2 Pyrolysis temperatures and characteristic masses for the simultaneous detection of chromium and manganese with different chemical modifiers

Chemical modifier		$T_{pyrolysis}$ (°C)		m_o (pg)	
	mass (μg)	Cr	Mn	Cr [a]	Mn [b]
None	-	1200	1100	6.0	2.6
$Mg(NO_3)_2$	3	1500	1300	7.8	4.6
$Mg(NO_3)_2$	10	1500	1300	10	6.5
Pd	5	1500	1300	11	4.3
Pd	10	1500	1300	13	6.8
Pd + $Mg(NO_3)_2$	5+3	1500	1400	12	6.4
Rh	5	1600	1200	11	7.5
Rh	10	1600	1200	11	7.7
Rh + $Mg(NO_3)_2$	5+3	1600	1300	11	7.9

[a] 3.6 pg [16], 3.0 pg [11] and 5.4 pg [18] without chemical modifier, 3.3 pg [12, 17] and 3.2 pg [16] with $Mg(NO_3)_2$, and 3.0 pg [16] with Rh as chemical modifier.
[b] 4.1 pg with $Mg(NO_3)_2$ as chemical modifier

The characteristic masses attained for chromium in the simultaneous multielement mode (Table 2) were always higher than those previously reported in the literature for monoelement GFAAS [11, 12, 16, 17, 18]. Under the same conditions, the calculated characteristic masses for manganese (Table 2) were also higher than that previously reported in the literature [26].

Addition and recovery tests of 2.5 μg L^{-1} of chromium and manganese in urine solution (1+1) in the presence of 2.0% (v/v) HNO_3 + 0.05% (m/v) Triron X-100 were used to select the chemical modifier. Without chemical modifier and adopting 1100 °C as pyrolysis temperature (hold time=30 s), the chromium and manganese absorbance signals were affected and the background was high for both elements. In the presence of urine (1+1) the thermal stability and the sensitivity of manganese were affected by 5 μg Pd, 10 μg Pd, or 5 μg Pd + 3 μg $Mg(NO_3)_2$. Attenuation of the background signal occurred only above 1100 °C, when the absorbance signal of manganese was lower due to volatilization in the pyrolysis step. Furthermore, the addition of these chemical modifiers produced poorly shaped and noisy peaks for chromium and the background was always high, as also observed by Burguera et al. [17]. In spite of the higher pyrolysis temperature for manganese (1400 °C) resulting from addition of 5 μg Pd + 3 μg $Mg(NO_3)_2$, the

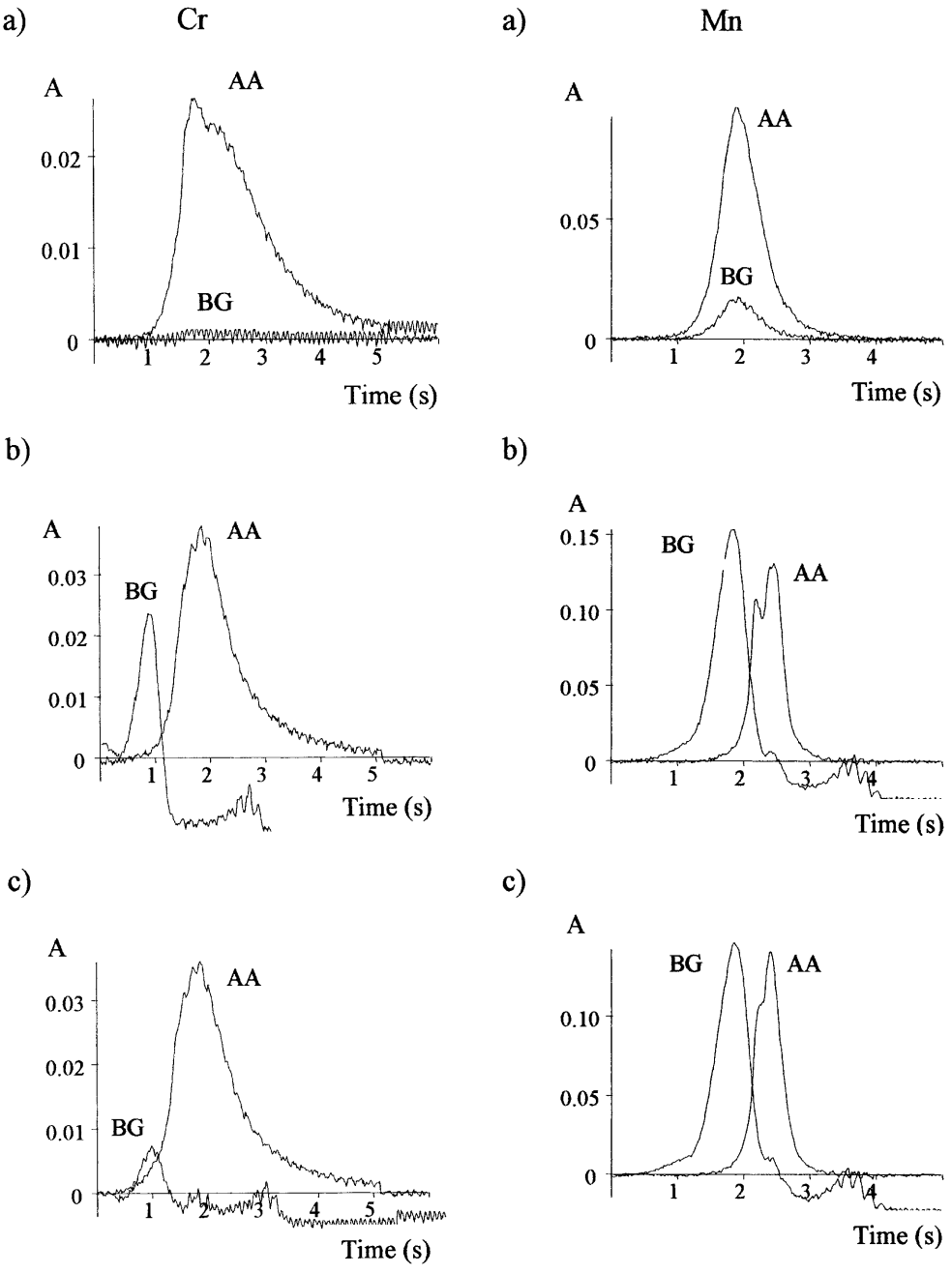

Fig. 1 Atomic absorption (AA) and background (BG) signals for simultaneous atomization of 2.5 μg L^{-1} of chromium and manganese: (**a**) 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100, (**b**) and (**c**) urine (1+1) + 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100. Heating program: **(a)** and **(c)** with two pyrolysis steps (800 °C, hold time=20 s and 1300 °C, hold time=15 s), **(b)** with one pyrolysis step (1300 °C, hold time=15 s)

recovery of this element was unsatisfactory (43%). The worst recovery for chromium and manganese was observed when 5 μg Rh, 10 μg Rh, or 5 μg Rh + 3 μg $Mg(NO_3)_2$ were injected with reference solution prepared in urine media. The high chloride content of the reagent employed to prepare the modifier solution ($RhCl_6$) and the chloride content of urine depressed the absorbance signal of chromium and manganese, probably owing to the formation of volatile chromium- [31] and manganese-chloro compounds [30]. According to the literature, at pyrolysis temperatures below 700 °C manganese can be lost by formation of manganese chloride in the gas phase, whereas above 700 °C volatilization of manganese chloride take place during the pyrolysis step [5, 31]. The chemical modifier 3 μg $Mg(NO_3)_2$ led to the best recovery for 1.0 μg L^{-1} of chromium and manganese added to different urine samples (95%, RSD=5.4%) and (92%, RSD=5%), respectively. Consequently, this chemical modifier was chosen to improve the determination of chromium and manganese in urine using aqueous calibration procedure.

The maximum pyrolysis temperatures achieved for chromium and manganese were 1500 °C and 1300 °C, respectively. The choice of pyrolysis temperature adopted for simultaneous determination was dictated by the thermal stability of manganese. The atomization temperature (2500 °C) was chosen on the basis of the higher chromium absorbance signals.

Table 3 Results for chromium and manganese determination in urine using aqueous calibration and 3 μg $Mg(NO_3)_2$ as chemical modifier

Chromium (μg L^{-1})			Manganese (μg L^{-1})		
Without addition [a]	With addition	Recovery (%)	Without addition [a]	With addition	Recovery (%)
0.20±0.02	1.0	90	0.80±0.06	1.0	92
0.28±0.01	1.0	102	0.62±0.10	1.0	95
0.62±0.01	1.0	91	1.80±0.01	1.0	82
0.50±0.05	1.0	95	1.64±0.20	1.0	96
0.40±0.07	1.0	85	1.30±0.15	1.0	89
0.70±0.04	2.5	120	0.60±0.08	2.5	84
0.60±0.09	2.5	104	0.80±0.06	2.5	86
2.10±0.10[c]	2.5	84	<LOD	2.5	80
<LOD[b]	2.5	124	<LOD	2.5	88
2.00±0.08[b,c]	2.5	108	0.40±0.04	2.5	90

[a]Values±Standard Deviation (n=3)
[b]female
[c]cigarette smoker
(LOD) Limit of Detection

The heating program proposed has two pyrolysis step: one using moderate temperature (800 °C, hold time=20 s) and the other using higher temperature (1300 °C, hold time=15 s) (Table 1). When the first pyrolysis step was implemented a reduction of the background signal was observed for chromium (Fig. 1c). However, in the absence of this step, using only one pyrolysis step (1300 °C, hold time=30 s) the background of correction (BOC) change during the measurements for chromium was higher for manganese (Fig. 1b). The correct choice of time and temperature of the pyrolysis step is essential for overcoming the matrix interference and assuring adequate conditions for analysis. The times adopted for the first and second pyrolysis steps, 20 s and 15 s, were sufficient to produce the best recoveries, as discussed above. The hot-injection procedure (100 °C) was important to guarantee good sampling, minimizing the foam formation inside the THGA tube and also to shorten the drying step. The heating program time was 94 s and the total cycle time including sampling, heating, and data collection was approximately 130 s. With this heating program, it was possible to perform 28 simultaneous determinations of chromium and manganese per hour.

Calibration curves for chromium and manganese were obtained for aqueous reference solutions using the heating program given in Table 1. The linear range up to 3.0 μg L^{-1} for both elements in 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100 was adopted on the basis of the chromium and manganese levels in urine [1]. The slopes and linear correlations of the chromium and manganese curves were (slope=0.01110, r=0.99519) and (slope=0.01894, r=0.99973), respectively.

The characteristic masses attained using 3 μg $Mg(NO_3)_2$ as chemical modifier, based on five measurements of consecutive integrated absorbance and for 20 μL of sampling solutions, were 7.8 pg (RSD=4.0%) for chromium and 4.6 pg (RSD=2.6%) for manganese. The limits of detection were 0.08 μg L^{-1} for chromium and 0.16 μg L^{-1} for manganese, calculated according to $3s_{blk}/m$ (n=20), where s is the standard deviation of the blank measurements and m the calibration curve slope. The blank solution [2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100] was taken through the whole sample preparation procedure and analyzed together with 3 μg $Mg(NO_3)_2$ as chemical modifier. The limits of detection are very close to the chromium and manganese urine levels in a normal individual, i.e. about 1.0 μg L^{-1} [1]. Thus, the determination of these elements in urine should be performed with minimal sample dilution and manipulation to avoid contamination. Urine dilution (1+1) with 2.0% (v/v) HNO_3 + 0.05% (w/v) Triton X-100 was sufficient to obtain satisfactory sensitivity and low background signals. The THGA tubes allowed at least 350–400 firings without loss of sensitivity.

Ten different urine samples with and without addition of 1.0 μg L^{-1} and 2.5 μg L^{-1} of chromium and manganese were analyzed by using an aqueous calibration procedure (Table 3). The results were based on three replicate determinations of the same sample. Chromium and manganese concentrations found in urine from eight volunteers were in accordance with those considered as normal in healthy people [1]. For the smokers among the volunteers, the concentrations of chromium found in the urine were higher than those for other volunteers. It is known from the literature that the chromium concentration in the urine increases with tobacco consumption [32].

Conclusion

Direct and simultaneous determination of low concentrations of chromium and manganese in urine using aqueous calibration solutions can be performed by SIMAA. The limits of detection (0.08 μg L^{-1} for chromium and 0.16 μg L^{-1} for manganese) are sufficiently low to permit determination of these elements in urine from non-exposed and occupationally exposed subjects. This simultaneous method could be used for monitoring chromium and manganese levels in the urine of exposed individuals, with reduced instrument operation time, less frequent replacement of graphite tubes, and lower consumption of reagents and sample. The proposed procedure allows 28 determinations per hour, and requires only minimum sample preparation, thereby reducing the risk of contamination.

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