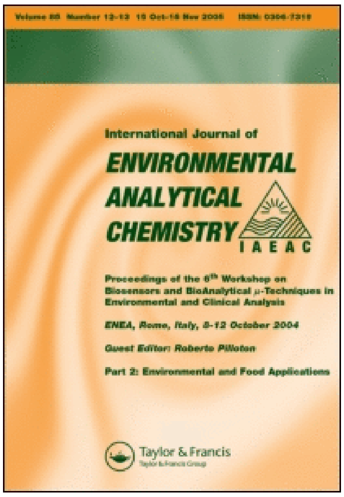

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Determination of Heavy Metal in Drinking Waters by X-Ray Spectroscopy

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Concentrations of trace elements in some drinking waters were determined using the X-ray emission spectroscopy. Water samples were collected near Rijeka, the most industrialized centre in the northern part of the Yugoslav coast, to find out if concentration of heavy metals in water are within permitted limits.

Since concentrations of heavy metals in natural water are quite low, it was necessary to preconcentrate the water before the analysis.

Two techniques of water samples preparation were used depending on the elements to be analyzed:

i) precipitation by the APDC (amonium-pyrrolydine-dithiocarbamate) (for Fe, Ni, Cu, Zn, As, Pb and Hg).
ii) complexation with the APDC followed by the adsorption on activated carbon (for U).

KEY WORDS: Heavy metals, drinking water, X-ray spectroscopy, precipitation, complexation, preconcentration

INTRODUCTION

The monitoring of elemental composition of drinking water is of great importance. Human health closely depends on the concentration of trace elements in drinking water, and therefore there exists criterions that should be satisfied.[1,2,3]

TABLE I

Maximal concentrations (ppm) of some metals in waters according to the law for water regulation in SR Croatia

Element	Concentration (ppm)
As	0.05
Cu	0.01
Zn	0.10
Ni	0.05
Pb	0.01
Fe	0.30
Hg	0.0002

Low concentrations of toxic elements (Hg, Pb, As, Cd, U) can be dangerous for humans, while some other trace elements can cause diseases when present in excess.[1] High environmental pollution causes changes in concentrations of trace elements in soil and in natural water, as well as in the drinking water. A law has been regulated in the SR Croatia stating maximal allowed concentrations of some elements and substances in water[4] (see Table I).

A programme for the elemental analysis of all drinking waters from the Rijeka area has been made, and the first investigations are already performed. Sample preparation techniques were established and concentrations of many trace elements were simultaneously determined by X-ray spectroscopy.

Samples were prepared:

i) using complexation by amonium-pyrrolydine-dithiocarbamate (APDC) (for the analysis of Fe, Ni, Cu, Zn, Pb, As, Mg);

ii) using complexation with APDC followed by the adsorption on activated carbon (AC) (for analysis of U).

EXPERIMENTAL

Sampling

Drinking water samples were collected in the Istra peninsula, the city of Rijeka and Gorski kotar (see Figure 1).

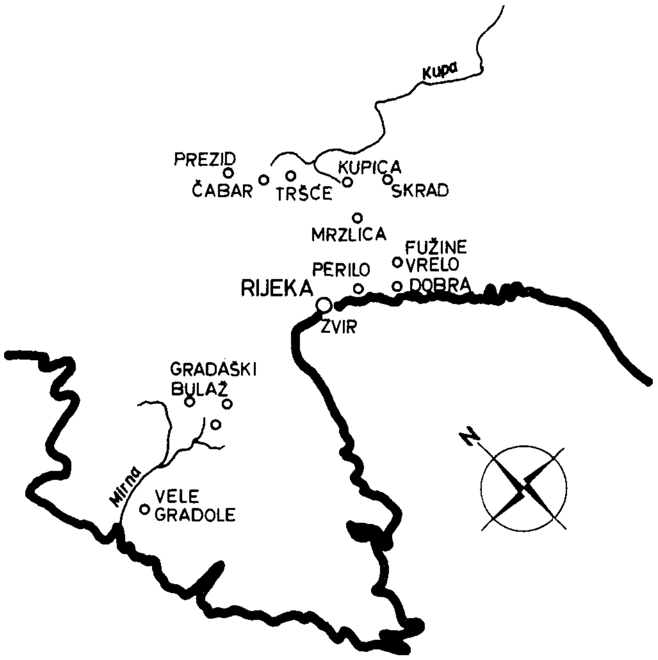

FIGURE 1 Locations of sampling.

In order to get accurate results, special attention was paid to the sampling procedure, the sample storage and the transport.

Water contamination, during sampling, was avoided using a teflon sampler.[9] From this sampler, water (1 l) was poured directly into clean polyethylene containers, and 6–7 ml of 10% HNO_3 were added to prevent container wall losses of heavy metals. Samples were immediately transported to the laboratory and prepared for the analysis. Once prepared and adequately stored the samples can wait for a longer time to be analysed.

Sample preparation

The precipitation procedure with APDC (a nonspecific multi-element reagent) is a fast and simple method of sample preparation.[2,5–8,13]

It is suitable for the analysis of the most common trace elements in fresh water (Fe, Ni, Cu, Zn) and of some toxic elements (Hg, Pb, Cd and As). Complexes of these elements with APDC are very stable and show low solubility in water, so they can be trapped on a membrane filter (Millipore—0.22 μm pore size) which serves as a target holder.

For target preparation 250 ml of water were used. After adjusting the pH to the value of about 3,[5,7] 2 ml of 1% APDC solution were added, mixed, and allowed to stand for about 20 min. After filtration, the suspension was air-dried and protected by Formvar. The target thickness (surface density) was usually less than 1 mg/cm^2.

For uranium determination a complexation method with subsequent adsorption of the U–APDC complex[10,11,12,13] on activated carbon (30 mg per sample) was used. The mixture was shaken for an hour, filtrated and protected by Formvar foil. The thickness of the targets varied from 16–18 mg/cm^2, and the matrix consisted mainly of C ($\sim$96%) and S ($\sim$3%). Standards for uranium were prepared in the same manner and a calibration curve was obtained (Figure 2).

Measurements

Elements in the samples were excited by monoenergetic beams of Mo-K$_\alpha$ and K$_\beta$ lines through a collimator of pure Al with an aperture of 4.5 mm in diameter and 22 mm in length. The working conditions for the Philips Röntgen apparatus with the Mo-anode were $V = 34$ kV, $I = 24$ mA, $t = 900$ s, (dead time was $\leq 2\%$). A Si–Li detector with the energy resolution of 180 eV at $E = 5.9$ keV was used. The geometry of the arrangement is shown in Figure 3.

The effective (irradiated, and visible by detector) surface of the sample was about 0.25 cm^2 (0.25 ± 0.02 cm^2). The minimum detection limits (MDL)[14] for some elements are shown in Figure 4. The MDL for uranium is about 0.024 μg (0.096 μg/cm^2) (or about 0.4×10^{-3} ppm, if 250 ml of water was used for sample preparation).

The absorption of the U–L$_\alpha$ line in the sample was calculated to be equal or less than 4% and the matrix effects were neglected. The absorption of the Fe–K$_\alpha$ rays in the targets prepared using the APDC only, ($\rho d \leq 1$ mg/cm^2, and the main matrix constitutents are *S, N, C, H*) was calculated to be equal or less than 9%. The

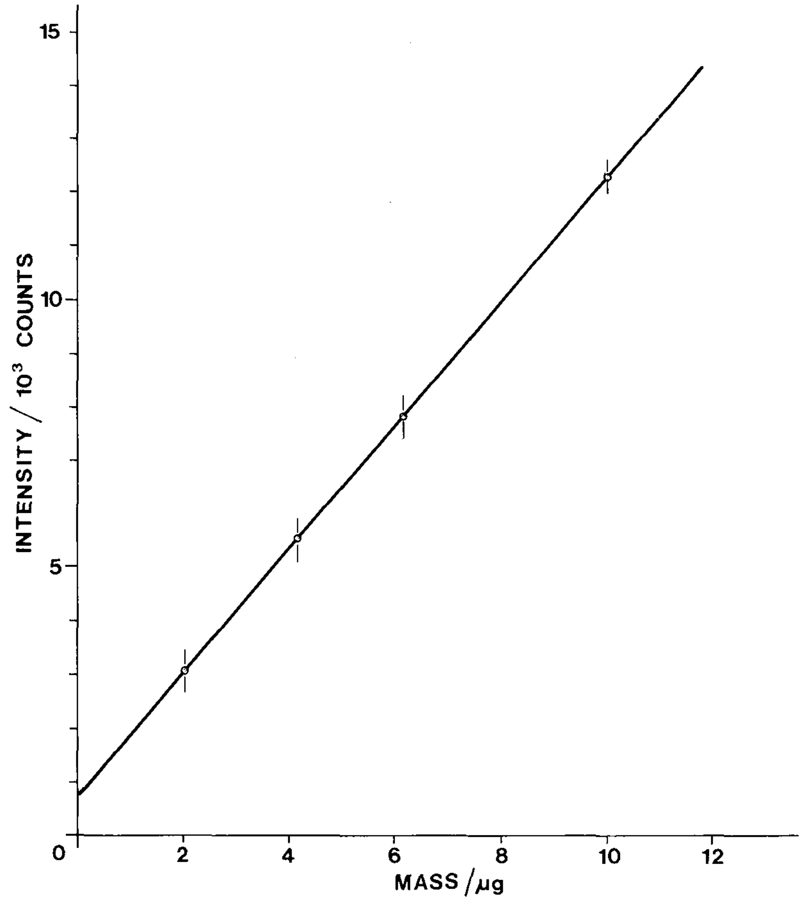

FIGURE 2 A calibration curve for uranium obtained by analysing standards with various uranium concentration (irradiating conditions were $I=18\,\text{mA}$, $V=34\,\text{kV}$).

attenuation for the other elements analysed was still lower (Zn ≈ 4%, Pb ≈ 3% ...). However, standards were prepared in the same way as samples, and the attenuation was approximately equal.

$$m_i = \frac{I_i \times t_i}{\varepsilon_i' \times t_i'} \qquad \varepsilon_i = \frac{I_i(\text{standard}) \times t_i'}{m_i(\text{standard})} = \varepsilon_i' \times t_i'$$

$$C_i(\text{water}) = m_i \times 0.25\ (10^{-3}\,\text{ppm}) \qquad t_i \approx t_i'$$

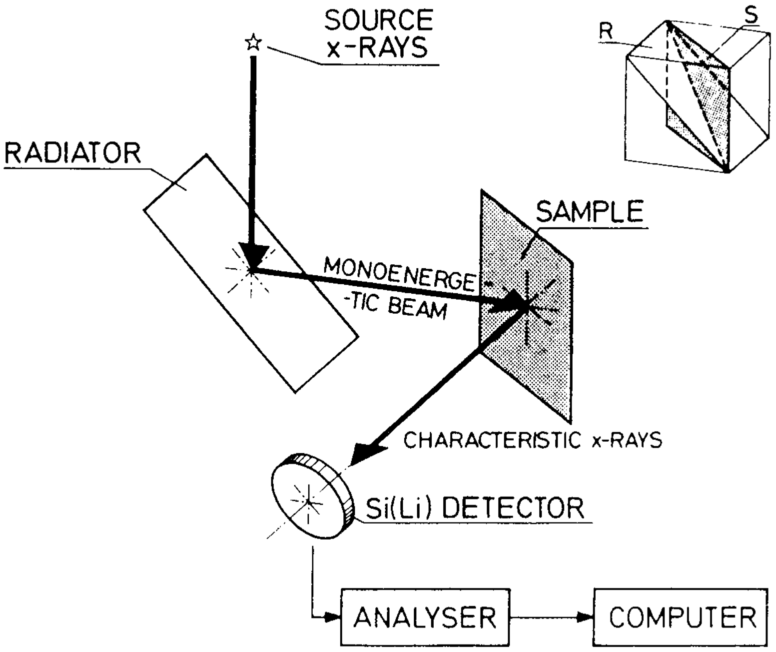

FIGURE 3 Geometry of sample irradiation system.

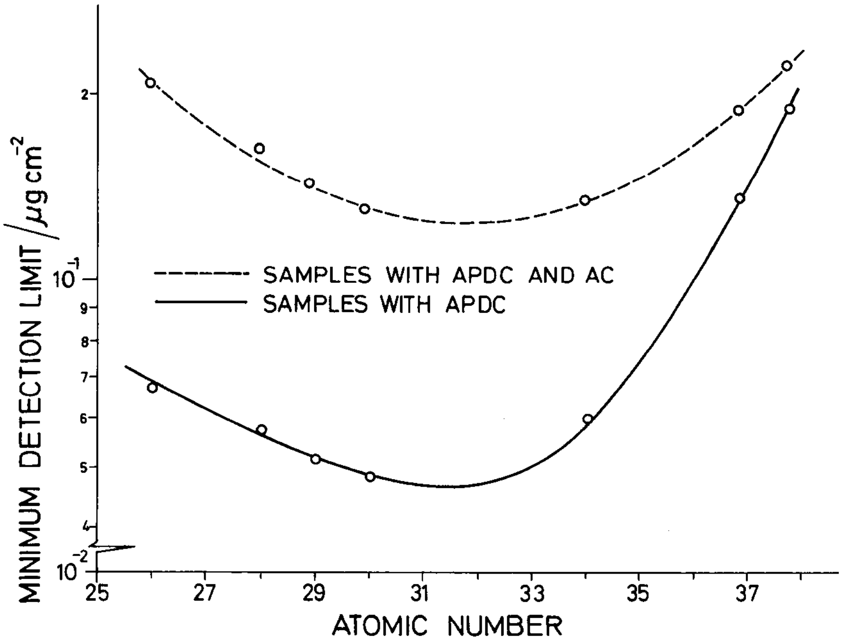

FIGURE 4 Minimum detection limit for elements.

where

m_i = amount of the element (i) in target (standard) (μg)
C_i = concentration of the element (i) in water (10^{-3} ppm)
I_i = count rate for the line of the element (i)
t_i = attenuation correction coefficient.

Spectra were approximated by Gaussian shaped peaks and polynomial background using the chi-squared optimization method.

RESULTS AND DISCUSSION

Samples prepared with AC were suitable for the analysis of uranium, but not for the analysis of the other elements in water, because many of them are present in the AC as heterogeneously distributed impurities. In Table II are given the values obtained analysing AC alone.

Concentrations of trace elements in some drinking waters analysed are shown in Table III. Samples were prepared using both of the techniques described (depending on the elements to be analysed). Concentrations of uranium higher than MDL were determined in just a few water samples, mainly those collected in Istra. Concentrations of iron and zinc widely ranged from location to location. In a sample collected in Gorski kotar (Prezid) mercury was found in concentration much higher then allowed. All these variations in concentration are probably influenced by ground constituents. On the other hand, somewhat higher concentrations of lead, copper and iron in the water from the cities of Bakar and Rijeka (Zvir) should be ascribed to pollution.

TABLE II
Concentrations of impurities (%) in AC

Element	Concentrations (%)
Fe	0.02 -0.05
Ni	0.005 -0.0009
Cu	0.0009-0.004
Zn	0.004 -0.008
Pb	0.005 -0.002

TABLE III

Concentrations of elements in some fresh waters (0.001 ppm)

Location	Fe	Ni	Cu	Zn	Pb	As	Hg	U
Zvir	46.3	7.90	2.18	5.1	1.6	0.3	0.4	<MDL
Perilo–Baker	85.6	2.0	1.6	2.2	0.6	0.1	0.3	<MDL
Dobra–Bakar	51.8	2.3	4.8	4.9	5.0	0.1	<MDL	<MDL
Dobrica–Bakar	41.2	6.2	2.6	4.2	0.8	<MDL	0.6	<MDL
Skrad	12.4	2.6	1.1	7.8	0.9	0.3	0.3	<MDL
Mrzlica	28.5	2.4	2.1	12.6	2.4	0.3	0.5	<MDL
Trsće	51.9	4.2	2.8	127.3	1.6	0.5	0.2	0.8
Prezid	13.2	2.3	1.9	56.7	3.4	0.5	6.6	<MDL
Čabar	29.1	7.4	1.8	24.7	1.2	0.1	0.5	<MDL
Kupica	79.7	1.3	1.5	2.7	0.8	0.2	<MDL	<MDL
Vele Gradole	66.7	0.5	2.3	4.2	1.8	<MDL	<MDL	0.80
Ponte Porton	635.4	1.7	3.1	21.5	3.9	<MDL	<MDL	0.70
Bulazić	258.3	2.8	5.3	8.8	2.4	<MDL	<MDL	<MDL
Pišmanjak	920.7	3.7	2.2	9.2	1.4	0.9	0.9	1.3
Murari	76.8	1.8	4.9	12.0	4.5	1.4	<MDL	0.7

The results obtained are preliminary. The programme will continue with samples being collected at different times of the year, to check seasonal effects (all the samples analysed to data were taken in autumn). Water samples from the other parts of that area will be also collected (the islands of Krk and Cres and some other locations in Gorski kotar and Istra) to obtain a complete picture of heavy metals concentrations in the drinking water of the north-west part of Croatia.

CONCLUSIONS

With sample preparation techniques developed, the analysis by X-ray spectroscopy presents a suitable method for a simultaneous determination of many trace elements concentrations in water.

The analyses of fresh water samples collected from a large area and during a longer period of time will allow to get a better view into effects of industry, and natural ground constituents in particular on the elemental concentrations in drinking water.

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