X-RAY SPECTROMETRY
X-Ray Spectrom. 2002; **31**: 259–263
DOI: 10.1002/xrs.533

XRS

Analysis of waste water by x-ray fluorescence spectrometry†

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Received 20 February 2001; Accepted 21 August 2001

Methods of specimen preparation for the x-ray fluorescence analysis of water are described. For direct determination of impurities in waste water samples, quasi-solid specimens based on gelatin (agar) are proposed. Such specimens may also be used after extractive enrichment of impurities and their re-extraction into the aqueous phase. For organic specimens, those in the form of organogels or thin polymer films can be obtained directly. For group impurity concentration it is proposed to use low-temperature directed crystallization of water with subsequent obtaining of glassy saccharose-based specimens from aqueous concentrates. The techniques developed were applied to determine Ag, As, Bi, Cd, Co, Cu, Fe, Ga, Ni, Pb, Se and Zn impurities in waste waters. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

Industrial, household and atmospheric waste waters contain a variety of dissolved or suspended inorganic and organic impurities. The qualitative and quantitative composition of such elements must be subjected to severe control. Prior to being drained into water reservoirs, waste waters are passed through different purification units, and the purification efficiency is estimated by analysis. The analysis is performed for both high-concentration unpurified sewage and dilute solutions with compositions close to that of surface water.

For the determination of inorganic components in waste waters, promising methods are those which allow the simultaneous determination of a large number of elements over a wide concentration range, irrespective of the form of their existence in the objects under investigation. Among such methods, x-ray spectrometry should be mentioned; however, it is used for this purpose much more rarely than, e.g., inductively coupled plasma atomic emission spectrometry (ICP-AES). This is explained by the fact that the method is not sensitive enough with respect to certain very harmful contaminants of water. Moreover, direct x-ray fluorescence (XRF) analysis of solutions entails technical difficulties and is characterized by essential errors of the results.[1] Direct XRF analysis of solutions is used only to determine elements that have characteristic emission lines that can penetrate the Mylar window of the specimen holder. Most liquids cannot be analysed under vacuum. Bubbles released from solutions due to inadequate cuvette filling and heating of the solution give rise to certain problems. They are particularly troublesome when the extraction source (tube) is located above the cuvette. Furthermore, it is difficult to maintain a constant distance between the surface of the liquid sample and the x-ray tube anode. The expansion of the Mylar film of the cuvette also changes the distance between the anode and the specimen and causes errors. Nevertheless, x-ray spectrometry method has been applied to the direct determination of zirconium in industrial solutions[2] and of strontium in nuclear engineering waste.[3]

To obtain solid specimens more suitable for the analysis and to lower the limits of detection of elements in solutions, the following techniques are conventionally used: drying of the solutions on paper filters[4] or on other solid substrates,[5–9] coprecipitation of phosphates of the cations to be determined on iron(III) phosphate[10,11] or on pyrrolidine dithiocarbamates of some metals;[12,13] in manufacturing solutions bromide is precipitated in the form of AgBr.[14] Note that it is difficult to obtain homogeneous specimens with satisfactory working surfaces after water evaporation or concentration of impurities by precipitation or coprecipitation methods. Moreover, the introduction of coprecipitators makes the element composition of the specimens more complex. Besides, extraction of the determined impurities by precipitation or coprecipitation is a labour-intensive procedure. Drying of considerable amounts of solutions on paper filters is even more laborious and prolonged.

To eliminate the drawbacks in waste water analysis, in this paper we propose the use of gelatin gels, saccharose-based glasses or polymer films as specimens, and to combine the analysis with preliminary extraction or concentration by crystallization of the elements under determination.

EXPERIMENTAL

To determine impurities directly in waste waters using gel-like specimens, ground gelatin (0.25 g) or agar (0.05 g) and the water solution to be analysed (2 ml) were placed in a glass crucible, mixed there and kept for 30 min for swelling to occur. Then the solution was heated by means of an electric furnace until the mixture became homogenized (but not boiling) and was poured into a Teflon cuvette. After

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†Special Issue on X-Ray Methods in Countries of the Former Soviet Union.

10 min the cuvette containing the solidifying solution was rapidly turned over on to a glass plate covered with a Teflon film. After 15 min, the gel-like specimens together with the cuvette were placed in the sample holder of a spectrometer to measure the intensity of x-radiation.

The thickness of the gelatin- or saccharose-based specimens obtained was limited by the height of the sample holder (6 mm). For the investigated elements it correspond to the unsaturated layer. However, this did not cause additional errors since the said thickness was well reproduced.

Ag, Bi(III), Cd, Cu(II), Fe(III), Ni, Pb(II) and Zn determination in waste waters, preceded by their extractive enrichment and re-extraction in an aqueous phase to obtain gel-like specimens, was carried out according to the following routine. A 0.5–11 volume of the analyte water and 10 ml of 30 wt% tartaric acid solution were poured into a separating funnel, then 2–3 drops of a 0.1 wt% ethanolic solution of phenol red, 25 wt% ammonia solution (to make the colour of the solution pink) and 5 ml of 10 wt% sodium diethyldithiocarbamate solution were added, and finally 5 ml of chloroform were introduced. Heavy metal carbamates were extracted by four 5 ml portions of chloroform during 5 min. The extracts obtained were placed in another separating funnel containing 0.5 ml of tartaric acid solution, 0.5 ml of 10 wt% mercury(II) nitrate solution and 1–2 drops of phenol red and ammonia solution (to make the colour of the mixture pink). Re-extraction of the metals from the organic into the aqueous phase was performed during 5 min, then the organic phase was poured into a special glassware for mercury waste and the aqueous phase was placed in a 2 ml measuring flask and diluted to volume with distilled water. Then a gel-like sample was reduced and the resultant concentrate was used for XRF analysis.

For the determination of impurities in waste waters by the technique comprising their preliminary extractive enrichment and obtaining the specimens in the form of organogels, the procedure was as follows. The extract under analysis (0.75 ml), surfactant (0.075 g or 0.1 ml) and a warm solution of 10 wt% gelatin (1 ml) were placed in a 10–20 ml weighing bottle, which was then covered with a cap and shaken vigorously. Subsequently the mixture was poured into a Teflon cuvette. After 10 min, the cuvette with the solidifying solution was turned over on to a glass plate covered with Teflon film. After 15–20 min the specimens obtained were used for measurements of characteristic x-radiation.

For the technique of impurity determination combined with extractive enrichment and obtaining specimens in the form of polymer film, 0.1 g of dry Carbosil-70 polymer (a block copolymer of polysiloxane and polycarbonate) was added to the organic extract. The solution obtained was placed in a Teflon cuvette with dimensions corresponding to those of the sample holder of the x-ray spectrometer. After most of the chloroform had evaporated, the cuvette was placed in a Petri dish, covered and kept there until the solvent had completely evaporated. As a result, a film containing micro-quantities of the analyte element and the polymer was formed at the bottom of the cuvette. To obtain a high-quality polymer film from the extract, the evaporation procedure was performed in a chloroform vapour atmosphere (chloroform contained in a covered Petri dish was placed close to the cuvette with the extract).

In all the cases extractive enrichment was quantitative, i.e. the degree of recovery was practically equal to 100%.

To determine impurities by the technique comprising their preconcentration by crystallization and obtaining glassy saccharose-based specimens, low-temperature directed crystallization of ∼100 ml of water was effected. In this case saccharose (1 g) was added into the analyte concentrate (∼1 ml) and this mixture was heated for 3–5 min to obtain caramel. After cooling the latter, the specimen was formed.

In most cases, preconcentration by crystallization was partial and the degree of recovery decreased with increase in the degree of mineralization of the water under investigation. The impurity concentration in the analyte water was calculated using the distribution coefficients determined experimentally for each type of water. These coefficients are independent of the nature of the impurity.[15]

In the case of extractive enrichment, if it is necessary, the complexes of the analyte elements with organic substances can be decomposed by different techniques, in particular by UV or ultrasonic methods.[16] Preconcentration by crystallization does not require such decomposition of the complexes formed by the analyte elements with organic ligands.

To measure the intensity of characteristic x-radiation we used portable spectrometers, SPARK-1 and Spektroskan (NPO Spektron, St. Petersburg, Russia), with Johansson x-ray optics, BS-1 type low-power fine-focus x-ray tube with Ag anode and LiF |002| crystal analyzer, and also a VRA-30 automated stationary spectrometer (Karl Zeiss, Jena, Germany) with Soller x-ray optics, high-power x-ray tube with massive Mo anode and lateral radiation output, LiF |002| crystal analyzer, 12–50 kV voltage across the tube and 20–50 mA current.

RESULTS AND DISCUSSION

Addition of gel-forming substances, e.g. gelatin or agar, to the solutions under analysis with subsequent heat treatment results in an increase in their viscosity. Such a transformation of liquids into quasi-solids provides specimens suitable for use for XRF analysis of solutions. In this case measurements may be carried out on spectrometers meant for solids. The compact, elastic specimens obtained conform to the shape of the cuvette in which they solidify and hold such a shape after being taken out of the cuvette. The degree of working surface purity is easily reproducible, is defined by the roughness of the forming surface and under optimum conditions corresponds to that of a polished surface.

The technique is directly applicable to waste water analysis. The presence of finely dispersed suspended particles or of substances which form colloidal solutions as well as organometallic compounds is not an obstacle for making quasi-solid specimens. Such specimens can also be obtained from aqueous re-extracts after extraction preconcentration of the elements to be determined.

As shown by special experiments, addition of quinhydrone favorably influences the thermal stability and radiation resistance of gelatin gels. In particular, their softening temperature increases from 35 to 75 °C and the time of radiation-induced softening of the gel increases from 60 to >400 s ($I = 20$ mA, $U = 25$ kV). The optimum conditions for obtaining gelatin gels were established to be the following: pH = 1–10, concentrations of gelatin and quinhydrone 10 and 2 wt%, respectively, and softening temperature close to room temperature (more exactly, lower than 24–26 °C, at which a new metastable phase of gelatin is formed).

To investigate the quality of the working surface of quasi-solid aqueous specimens, several similar specimens were produced on the basis of gelatin or agar containing 10 mg ml^{-1} of copper. Then the intensity of characteristic CuKα radiation was determined. The measurement results are presented in Table 1. The theoretical error of pulse counting is calculated from the expression $S_{r,1} = 1/\sqrt{N}$ (where N is the number of pulses, equal to 40 000 for VRA-30, 8000 SPARK-1 and Spektroskan spectrometers), $S_{r,2}$ is the experimental measurement error on repeated placing of the same specimen in the spectrometer sample holder and S_r is the total analysis error for the independently obtained specimens of the same composition.

The comparison of the $S_r^2/S_{r,1}^2$ and $S_r^2/S_{r,2}^2$ ratios with the Fisher coefficients presented in the last column of Table 1 shows that the contribution of the specimen preparation procedure to the total analysis error is practically zero, and the difference between the values of the calculated and experimental errors is caused by instrumental factors.

The characteristics of the method developed for XRF analysis using different calibration techniques are shown in Table 2.

As can be seen, the high quality of gel-like specimens allows one to carry out XRF analysis using different calibration techniques, in particular the external standard method.

The characteristics of the method for heavy metal determination in purified waste water are presented in Table 3.

It is shown that the values of S_r do not exceed 0.07 and the systematic errors are negligible in accordance with the t-criterion.

Extractive enrichment followed by re-extraction allowed to make the XRF analysis of purified waste water of quality close to that of domestic water.

When using liquid–liquid extraction for preliminary concentration of the elements to be determined in waters, it is not necessary to return these elements into the aqueous phase by means of re-extraction. We propose two methods, which permit good specimens to be obtained immediately from organic extracts. One is based on the transformation of organic extracts into organogels, i.e. emulsions of ‘oil-in-water’ type, and the other method consists in obtaining thin polymer films from the extracts.

As is known, gelatin swells, dissolves and manifests the ability to form gels only in water or in one-phase organic aqueous systems. We have shown that brief shaking for 10–15 s and subsequent spontaneous cooling of organic extracts containing small amounts of aqueous gelatin solution and surfactant result in organogels with a melting-point higher than that of ordinary gelatin gels. Such organogels are formed in many organic solvents using a variety of surfactants, but, as in the case of powder specimens, the error of x-ray intensity measurement is lower for smaller particle sizes (Table 4). The

Table 2. Characteristics of the method developed for XRF analysis using quasi-solid specimens (with gelatin applied as a thickening agent) and the SPARK-1 spectrometer)

Sample analysed	Element to be deter-mined	Calibra-tion method	Concen-tration of the element (mg l^{-1})	Relative standard deviation (S_r) (%)
Solution after copper board etching	Cu	External standard	25–400	0.08
		Background standard	10–100	0.09
Waste from ZnSe production	Se	Internal standard Ga	4–10	0.1
Waste from GaAs production	Ga	Background standard	4–30	0.06
Purified waste water	Ag, Bi(III), Cd, Cu(II), Fe(III), Ni, Pb(II), Zn[a]	External standard	0.01–0.04	0.01–0.07

[a] The elements are extracted as diethyldithiocarbaminates by CHCl$_3$ and then re-extracted into the aqueous phase by means of exchange reactions with mercury(II) ions.

Table 1. Estimation of relative standard deviation of a single result for x-ray fluorescence determination of 10 mg ml^{-1} copper in water using gel-like specimens[a]

Specimen	Spectrometer	f	S_r	$S_{r,1}$	$S_{r,2}$	$S^2{}_r/S^2{}_{r,1}$	$S^2{}_r/S^2{}_{r,2}$	$F(f, f, P)$
Gelatin	VRA-30	5	0.008	0.005	0.007	2.6	1.3	5.0
Gelatin	SPARK-1	6	0.04	0.01	0.03	16	1.8	4.3
Gelatin	Spektroskan	7	0.05	0.01	0.04	25	1.6	3.9
Agar	SPARK-1	9	0.03	0.01	0.03	9	1.0	3.4

[a] External standard method; the degrees of freedom for S_r, $S_{r,1}$ and $S_{r,2}$ are the same and equal to f; the Fisher coefficient $F(f, f, P)$ corresponds to a unilateral confidence probability of 0.95.

Table 3. Characteristics of the technique of heavy metal determination in water after their extraction preconcentration with subsequent re-extraction[a]

Element	n	S_r (%)	$t(P,f)$	C_L(mg l^{-1})
Ag	9	0.01	$0.3 < t(P, f) = 2.3$	0.04
Bi	9	0.01	$0.3 < t(P, f) = 2.3$	0.01
Cd	9	0.01	$0.3 < t(P, f) = 2.3$	0.01
Cu	6	0.07	$0.7 < t(P, f) = 2.6$	0.04
Fe	6	0.06	$0.8 < t(P, f) = 2.6$	0.04
Ni	7	0.02	$1.5 < t(P, f) = 2.4$	0.02
Pb	9	0.01	$0.3 < t(P, f) = 2.3$	0.02
Zn	6	0.05	$0.6 < t(P, f) = 2.6$	0.04

[a] C_L is the determination limit, n is the number of experiments, S_r is the relative standard deviation of a single result, $t(P,f)$ is Student's t, $P = 0.95$ is the confidence probability and $f = n - 1$ is the number of degrees of freedom.

particle radius was determined using an optical microscope ruler.

It should be noted that the linear sizes of these particles depend on the nature of the surfactant and correlate with its hydrophilic–lipophilic balance, which may be calculated beforehand from reference data.

In addition to gel-forming thickening agents such as gelatin, some polymers soluble in the given organic solvent and able to form films on drying may be used for the preparation of specimens from the organic extracts. Poly(vinyl chloride), suggested earlier[15] for this purpose, does not provide a uniform distribution of the determined elements in the specimen. We proposed the use of Carboxyl-70 (a block copolymer of polysiloxane and polycarbonate), applied in medicine. Such specimens are homogeneous in composition and thickness, have a smooth mirror surface and may be stored in air for a long time. This allows XRF analysis calibration by the external standard method. Film specimens are stable even in high vacuum, and as a result the number of elements to be determined may be increased.

The method of total reflection (TXRF), which uses only specimens in the form of thin films, is characterized by low detection limits. In the process of water analysis it seems expedient to combine TXRF analysis with preliminary impurity concentration, e.g. the extraction of diethyldithiocarbamate complexes of chloroform followed by obtaining a thin polymer film, or to use the considered below method of directed crystallization in combination with evaporation of aqueous concentrates on a substrate.

Table 4. Properties of gelatin emulsions based on different surfactant and solvents

Emulsion	n[a]	Particle radius (μm)	S_r (%)
CPB[b]–butanol	6	10	0.06
CPB[b]–CCl_4	8	20	0.09
Sodium oleate–isoamyl alcohol	6	30	0.03
Neonol–CCl_4	11	35	0.08
Flotamine–$CHCl_3$	10	60	0.11
Phenoxol–n-octane	7	100	0.12
Succinol–n-hexane	9	150	0.13
Sodium oleate–CCl_4	5	150	0.16
Tween-80–CCl_4	9	200	0.33

[a] n = Number of experiments.

[b] Cetylpyridinium bromide.

Similarly to extraction, low-temperature directed crystallization is a promising method for impurity concentration for XRF analysis of waste waters. The characteristics of this automated group concentration (by 1–1.5-fold) method for impurities of different nature were considered in another paper.[17] Such an enrichment allows one to obtain aqueous concentrates of a small volume to be used for making a thin specimen for TXRF (see above) or glassy organic saccharose-based specimens. As in the case of gel-like specimens, the use of a hydrophobic substrate provides specimens with very smooth working surfaces. Note that such a method of specimen preparation results in 2- or 3-fold additional preconcentration of impurities due to complete water evaporation. Unlike gelatin specimens (gels and organogels) which lose water in the course of time and therefore may be used only on the day of their preparation, saccharose-based specimens can be stored in a desiccator for 1–2 months. They are stable in vacuum and so can be utilized for the determination of light elements. In particular, directed crystallization combined with the use of saccharose-based specimens may be applied for selenium determination in water.[18] The characteristics of the method are shown in Table 5.

Thus, technological solutions containing heavy metal impurities in amounts of tens of milligrams per litre can be used directly for preparing quasi-solid specimens for direct XRF analysis. The technique for their preparation is simple and rapid.

To determine impurities at the level of 0.01 mg l^{-1} in purified waste water, we propose to concentrate them by liquid–liquid extraction in the form of chelates and subsequent preparation of specimens by one of the proposed methods. It is possible to carry out re-extraction of impurities in an aqueous phase and to make a quasi-solid specimen; one can to prepare directly an organic specimen as an organogel from the organic phase; finally, it is possible to evaporate an organic extract with the addition of a soluble polymer to obtain a specimen in the form of a thin polymer film.

The first method is universal, although labour-intensive. When obtaining organo-gel specimens the errors may be relatively large since such specimens are not homogeneous

Table 5. Characteristics for the method of Se determination in waste water after crystallization preconcentration using saccharose specimens

Se added (mg l^{-1})	Se found (mg l^{-1})	n
1.0	1.0 ± 0.2	6
2.5	2.5 ± 0.2	6
10.0	10 ± 2	6
22.5	22.4 ± 0.7	4

$S_r = 0.08$, $C_L = 0.15$ mg l^{-1}.

in the strict sense. The method of preparing polymer films provides the highest sensitivity.

Preconcentration by means of directed crystallization is a comparatively slow process. On the other hand, owing to its universality, this method is applicable to those impurities which cannot be extracted in the form of chelates. It is expedient to combine this technique with the preparation of organic glassy specimens based on saccharose.

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