

# Specimen Preparation in X-Ray Fluorescence Analysis of Materials and Natural Objects

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Specimen preparation is the source of the largest errors in x-ray fluorescence analysis. This paper reviews recent publications which deal with various methods of specimen preparation for the analysis of powders, compacted samples and fused specimens, non-destructive analysis of solid samples, direct analysis of solutions, the use of quasi-solid specimens, measurements in 'thin layers' and various ways of concentrating impurities from solutions and gaseous phases. Based on the literature and the authors' own studies, the best procedures were selected. © 1998 John Wiley & Sons, Ltd.

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## INTRODUCTION

Specimen preparation is known to be the largest source of errors in x-ray fluorescence analysis (XRFA). At  $2 \times 10^6$  counts and an insignificant background level, the relative standard deviation ( $S_r$ ) is  $1/\sqrt{N} \approx 7 \times 10^{-4}$ , that is, 0.07% (rel.). In many analyses, however, the actual error exceeds the counting error by 1.5–2 orders of magnitude, the major source of error being specimen preparation. It is important to use techniques which do not produce such large errors.

In recent years, several reviews have been published which deal with specimen preparation for the XRFA of liquids,<sup>1,2</sup> water,<sup>3</sup> aerosols,<sup>4</sup> pulps,<sup>5</sup> films,<sup>6</sup> ferrous metallurgy products,<sup>7–9</sup> rocks,<sup>10</sup> minerals and ceramics<sup>11</sup> and various materials of natural origin.<sup>12</sup> Concentration methods preceding XRFA have been discussed<sup>13</sup> and various techniques for specimen preparation have been considered.<sup>14–17</sup>

This paper reviews and attempts to compare various specimen preparation methods reported in the literature mainly in the period from 1987 to 1996. The authors have selected the methods which, they believe, are the most suited for the various materials to be analysed.

## ANALYSIS OF POWDERS AND COMPACTED SPECIMENS

To analyse a homogeneous finely dispersed powder, it is placed often in a specimen holder (cuvette) with a Mylar window. However, it should be noted that the procedure using loose powder suffers from essential errors. This technique has been used to analyse geochemical materials,<sup>18–20</sup> polycrystalline ores<sup>21,22</sup> and catalysts based on  $\text{Al}_2\text{O}_3$ .<sup>23</sup> To determine mobile forms of toxic

elements in soils, an ammonium acetate buffer extraction was used; the filtrates were evaporated on powdered coal and then the dry residue was ground thoroughly and placed in a cuvette as mentioned above.<sup>24</sup> For such an analysis, the material is formed into a powder with a particle size of 20–100  $\mu\text{m}$ , which exceeds by several orders by magnitude the wavelengths of the analytical lines of characteristic radiation of chemical elements that are used. An increase in particle size leads to the growth of errors conditioned by the sample inhomogeneity and by the interaction of the characteristic emission (especially soft emission) with the substance under study. The application of this method to coarse-grained materials (chips)<sup>25</sup> cannot yield satisfactory results.

To avoid agglomeration of fine particles during grinding, it has been proposed that the above method is performed in a volatile organic solvent (ethanol).<sup>9,26</sup> 'Wet' grinding of material, however, does not always produce a sufficiently uniform grain size, and still requires extensive grinding times. As has been shown,<sup>27</sup> grinding with micro-admixtures of silicone liquids produces powders with optimum particle sizes.

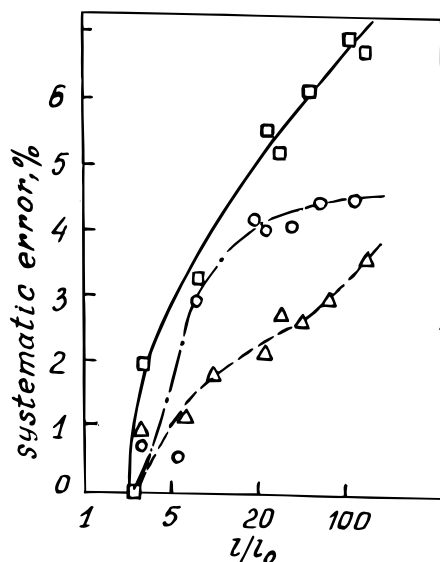
To determine sulphur in powdered specimens of rocks,<sup>28</sup> vacuum cuvettes of a special design were used.

Particle size non-uniformity is a source of error when analysing powders poured freely into a cuvette. The effect of particle size on XRFA results has been studied.<sup>29–33</sup> Systematic errors caused by the difference in granulometry of specimens under analysis and reference materials were evaluated<sup>33</sup> (see Fig. 1).

When analysing heterogeneous powdered materials, additional problems arise. It has been proposed to use in such cases experimental particle size distribution functions and also x-ray intensity dependences on the sample particle size for the elements under analysis;<sup>30</sup> this allowed the accuracy of the analysis of coarse-grained iron ores to be increased 1.5-fold.

Theoretical correction methods are often used to reduce the number of reference materials required when

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**Figure 1.** Relative systematic error vs. the ratio of mean linear dimensions of particles of specimens under analysis ( $l$ ) and reference materials ( $l_0$ ) for the determination of 0.4% of ( $\square$ ) Cr, ( $\circ$ ) Y and ( $\triangle$ ) Mo in powder samples of alum.<sup>33</sup>

performing XRFA of homogeneous powdered samples. It was found<sup>34</sup> that it is possible to extend this method to heterogeneous powders using sample density measurements.

The effect of surface roughness on XRFA results for powdered samples has been discussed<sup>32</sup> and it was shown that errors due to surface roughness can be minimized if measurements are performed at a steep take-off angle  $\geq 70^\circ$ . Unfortunately, most wavelength-dispersive spectrometers now in production do not allow the take-off angle to be varied.

The accuracy of powdered specimen analysis can be improved by using such a relatively simple precautions as compaction (pressing, briquetting).

From easily compacted materials specimens are made without adding plasticizers. Such techniques have been proposed for the analysis of sea salts,<sup>35</sup> lyophilized blood,<sup>36</sup> hay,<sup>37</sup> soils,<sup>38,39</sup> atmospheric dust,<sup>40</sup> rocks,<sup>41–44</sup> chopped plants,<sup>45,46</sup> soot,<sup>47</sup> some iron-containing materials,<sup>48,49</sup>  $ZrO_2$ ,<sup>50</sup> and slimes formed in the process of waste water purification.<sup>51</sup>

In the case of difficult-to-compact substances, various plasticizers are introduced into the sample. The plasticizers most widely used include boric acid<sup>52–55</sup> and its mixtures with calcium carbonate<sup>56</sup> or paraffin.<sup>57</sup> Iron–manganese concretions,<sup>52</sup> uranium(IV) oxide,<sup>54</sup> cast iron [the element to be determined, cerium, was coprecipitated as the oxalate with  $La_2(C_2O_4)_3$ ]<sup>55</sup> and various rocks<sup>56,57</sup> were analysed using this technique.

Powders compact well in the presence of cellulose (analysis of biological materials<sup>58</sup> and rocks<sup>59,60</sup>). Silicate enamel powders,<sup>61</sup> raw materials for blast furnaces<sup>9</sup> and rock ores and wood sawdust<sup>62</sup> were compacted with poly(vinyl alcohol). To analyse soils, polyethylene<sup>63</sup> and methyl methacrylate<sup>64</sup> were used as plasticizers. Analyses of metallurgical products with polystyrene,<sup>65</sup> of zinc sulphide using butyl methacrylate<sup>66</sup> and of geological objects with methyl methacrylate–butyl methacrylate copolymer<sup>67</sup> as additives have been described. The use of a triple copolymer

(acrylonitrile–butadiene–styrene) as the plasticizer has also been mentioned.<sup>68</sup> Coals and ashes were compacted using graphite,<sup>69</sup> soil samples with wax,<sup>70</sup> oxides of some elements with starch<sup>71</sup> and geological samples with a Bakelite phenolic resin.<sup>72</sup>

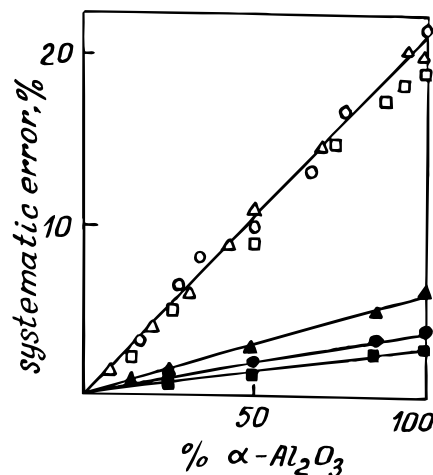
To avoid dilution with plasticizers of samples which do not press well, two-layered specimens are sometimes prepared. For example, slags of sulphidic nickel–copper ores<sup>73</sup> were compacted on a substrate of  $H_3BO_3$ , and the same technique was used for enamels<sup>74</sup> and loamy materials.<sup>75</sup> When analysing single crystals of mixed alkali metal halides<sup>76</sup> and those of fresnoite ( $Ba_2TiSi_2O_8$ ),<sup>77</sup> the ground sample was placed in an aluminium ring glued to a thin Mylar film, covered by a disc of preliminarily compacted Teflon and so subjected to compaction.

There are indications that the particle size of the powder to be compacted may influence the emission intensity of elements under determination, and therefore the initial material must be ground to a specified particle size. It has been shown<sup>28,78</sup> that, when compacted specimens are used, the emission intensity increases with increase in compaction pressure. Compaction at a constant pressure<sup>33</sup> allowed the elimination of the systematic error in the determination of dopants in aluminium–yttrium sulphate caused by differences in the granulometry of the samples to be analysed and reference specimens, provided that the particle size did not exceed 50  $\mu m$ .

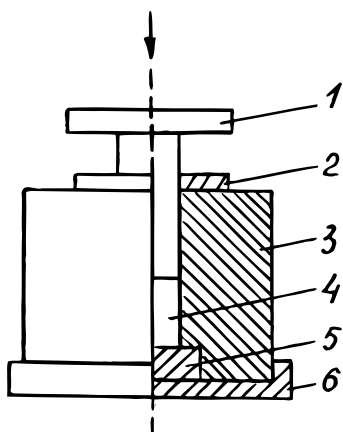
Still another source of systematic errors is phase composition differences between specimens to be analysed and reference materials (Fig. 2). Compaction of powdered samples under constant pressure results in a decrease in errors, but does not eliminate them completely.<sup>79</sup> It is known that the density of the specimen depends on its phase composition (the granulometry of the initial powder has a lesser influence). The dependence mentioned is described by the equation

$$\ln(\rho_{lim} - \rho) = \ln(\rho_{lim} - \rho_0) - AP \quad (1)$$

where  $P$  is the compaction pressure (MPa),  $\rho$  the specimen density ( $g\ cm^{-3}$ ),  $\rho_{lim}$  the material density in the



**Figure 2.** Relative systematic error vs. the content of  $\alpha-Al_2O_3$  in analysed specimens of aluminium oxide in the determination of 0.4% of ( $\triangle$ ,  $\blacktriangle$ ) Cr, ( $\circ$ ,  $\bullet$ ) Y and ( $\square$ ,  $\blacksquare$ ) Mo; open symbols, powder samples; closed symbols, specimens compacted at a constant pressure; reference materials made of  $\gamma-Al_2O_3$ .<sup>33</sup>



**Figure 3.** Diagram of a mould for making constant-volume specimens: 1 = plunger; 2 = split limiting ring; 3 = body; 4 = compacted material; 5 = liner; 6 = substrate.<sup>79</sup>

single-crystal state (for  $\alpha\text{-Al}_2\text{O}_3$  it is  $4.0 \text{ g cm}^{-3}$  and for  $\gamma\text{-Al}_2\text{O}_3$   $3.4 \text{ g cm}^{-3}$ ),  $\rho_0$  the powder free-fall density depending on its granulometric composition ( $\text{g cm}^{-3}$ ) and  $A$  a constant characterizing the material compactibility.

According to Eqn (1), the compaction of a material having variable phase composition at a constant pressure should result in various density values of specimens so obtained which should have various intensities of characteristic emission at the same content of the element to be determined. To eliminate the error mentioned above, it was proposed<sup>79</sup> to compact specimens of constant volume which, provided the compact material mass is constant, results in specimens of a specified density, irrespective of the phase composition of the initial powders. For this purpose, a mould was used where the plunger movement was limited by a ring made of an essentially incompressible material (Fig. 3) and the compaction pressure imposed ( $P$ ) corresponded to the following:

$$\ln\left(\frac{\rho_{\text{lim}} - \rho_0}{\rho_{\text{lim}} - \rho}\right) / A < P < \frac{S_1}{S_2} \sigma \quad (2)$$

where  $S_1$  and  $S_2$  are the working surface areas of the thrust ring and the plunger ( $\text{cm}^2$ ), respectively, and  $\sigma$  is the elastic limit for the thrust ring (MPa).

The efficiency of the proposed specimen preparation technique is illustrated by the data given in Table 1.

**Table 1.** Results of chromium determination in aluminium oxide samples by XRFA<sup>79</sup>

Specimen composition <sup>a</sup>		Compaction of constant volume specimen		Compaction at constant pressure	
$\alpha\text{-Al}_2\text{O}_3$ (%)	$\gamma\text{-Al}_2\text{O}_3$ (%)	Cr found (%)	$\Delta^b$ (%)	Cr found (%)	$\Delta^b$ (%)
—	100	$0.40 \pm 0.01$	0	$0.33 \pm 0.01$	22
25	75	$0.40 \pm 0.01$	0	$0.34 \pm 0.01$	18
50	50	$0.40 \pm 0.01$	0	$0.36 \pm 0.01$	12
75	25	$0.40 \pm 0.01$	0	$0.37 \pm 0.01$	9
100	—	$0.40 \pm 0.01$	0	$0.40 \pm 0.01$	0

<sup>a</sup> Reference materials were made on the basis of  $\alpha\text{-Al}_2\text{O}_3$ .

<sup>b</sup>  $\Delta$  = Relative systematic error.

## FUSION

The metrological characteristics of XRFA procedures using powders and compacted emitters are acceptable if impurities and doping admixtures in materials and environmental objects are to be determined, but they do not meet the requirements of the precise determination of major components of functional materials with complex compositions. In similar cases, material remelting<sup>80–85</sup> or fusion of the substance to be analysed with a suitable flux<sup>9,86–132</sup> is used. Sometimes, if the alloys so obtained are inhomogeneous or tend to crack, they are subjected to regrinding and recompaction.<sup>88,126</sup>

Remelting is used, as a rule, to prepare specimens of not very high-melting point materials, including primarily metals, to homogenize the substance and to obtain a specimen of desirable shape and with smooth surface. Such a specimen preparation technique was used to analyse bronzes,<sup>80</sup> blister and electrolytic copper,<sup>81</sup> aluminium<sup>82</sup> and other metals.<sup>83</sup> Melting was performed using an a.c. arc<sup>82,83</sup> or induction furnace heating.<sup>81</sup> To obtain bronze specimens with a smooth surface, centrifugal casting was used.<sup>80</sup> Sometimes, more refractory materials are remelted, e.g. ilmenite-type titanium dioxide ore.<sup>84</sup> Easily fusible coal and oil tars were melted at about  $140^\circ\text{C}$  and then the surface of the specimen was cooled and shaped under a load on contact with a Mylar film placed on an aluminium plate.<sup>85</sup>

Since many materials cannot be remelted without decomposition and at reasonable temperatures, fusion with easily fusible fluxes is used more often in the practice of XRFA. Of course, sample dilution with the flux results in reduced analytical sensitivity. Therefore, fusion is used mainly in the determination of elements of the base and some dopants.

According to Claisse,<sup>86</sup> the ideal features of a fusion technique are simplicity, rapidly, retention of the elements to be determined, high limit of sample/flux ratio, wide range of element concentrations in the sample, applicability of fundamental parameters matrix corrections, production of glass disks that are not prone to cracking or sticking in the mould and crucibles that need no cleaning after each fusion.

The original Claisse technique was proposed 40 years ago and consisted in fusing the sample with borax and casing into a solid button.<sup>87</sup> Nowadays many variations of the original method in which fluxes based on borates with different admixtures are used.<sup>88–93,95–124,131,132</sup> Such fluxes were employed to analyse slimes in waste waters,<sup>51</sup> geological samples,<sup>88–93,95–104,132</sup> iron ores and slags,<sup>105,106</sup> ferroalloys,<sup>124</sup> raw materials for blast furnaces,<sup>9</sup> zeolites with rare-earth ions concentrated on them,<sup>107</sup> cements,<sup>108</sup> electrocorundum,<sup>109</sup> non-ferrous metallurgy products,<sup>110</sup> some single crystals and functional ceramics<sup>111–115,131</sup> and various metal oxides.<sup>117,118</sup> Sodium tetraborate,<sup>106</sup> lithium tetraborate,<sup>9,90,91,93,96,97,100–102,105,114</sup> lithium methaborate,<sup>92,98,104,110</sup> pure iron,<sup>94</sup> lithium metaborate and potassium pyrosulphate mixtures,<sup>117</sup> those of lithium tetraborate and metaborate<sup>89,93,95,99,107,118,119</sup>

and lithium tetraborate and carbonate,<sup>108,124</sup> of sodium tetraborate and lithium carbonate,<sup>109</sup> of lithium metaborate and  $\text{H}_3\text{BO}_3$ ,<sup>131</sup> of boron and bismuth oxides<sup>111–113</sup> and of lithium metaborate and tetraborate with barium oxide<sup>132</sup> were described to be used as fluxes.

In some cases, oxidants ( $\text{LiNO}_3$ ,<sup>89</sup>  $\text{HNO}_3$ ,<sup>98</sup>  $\text{NH}_4\text{NO}_3$ ,<sup>9,96,105</sup>  $\text{NaNO}_3$ ,<sup>9</sup>  $\text{Na}_2\text{O}_2$  and  $\text{NaNO}_2$ <sup>91</sup>), compounds of heavy elements reducing x-ray scattering ( $\text{Bi}_2\text{O}_3$ ,<sup>111,112</sup>  $\text{La}_2\text{O}_3$ <sup>118,119</sup>) and admixtures that lower the melt viscosity ( $\text{NaI}$ ,<sup>101</sup>  $\text{KI}$ <sup>9,109</sup>) were introduced into the flux composition.

Borate fusion is widely used, but the castings obtained need to be cooled slowly to avoid possible spontaneous cracking due to residual thermoelastic stresses. Therefore, specimens are sometimes prepared not in the form of glassy disks, but in the form of a large number of beads 1–3 mm in diameter.<sup>120–123</sup> Such a specimen preparation method is obviously associated with an additional error caused by x-ray scattering from the surface of the beads.

Phosphates, such as lithium metaphosphate with various additives<sup>125</sup> and sodium meta- and pyrophosphates,<sup>126</sup> are among the more seldom used fluxes. An advantage of these fluxes is their high reaction ability caused by the formation of phosphate complexes of transient metals which are the components of the substances under analysis. It has been shown<sup>128</sup> that the use of lithium metaphosphate as a flux for high-precision XRFA of oxide materials produces specimens in the form of homogeneous glass-like castings which do not require prolonged annealing or subsequent machining. It is possible to use this technique to produce specimens of various oxide materials by varying the admixture compositions (Table 2). A special

investigation<sup>129</sup> has shown that reference materials in the form of glass-like phosphatic specimens can be used after 18 months and even longer, provided that they are stored in a desiccator over phosphorus pentoxide. Using this specimen preparation technique, a procedure for calcium, strontium, bismuth, lead and copper determination in bismuth-containing superconducting ceramics was developed;<sup>130</sup> the procedure is characterized by insignificant systematic errors and very low random errors (for an individual result,  $S_r = 5 \times 10^{-3} - 7 \times 10^{-3}$ ).

Melt interaction with the crucible material and casting adhesion to the wall of the mould may cause serious difficulties in the course of glassy specimen preparation. Sometimes, the specimen is obtained in the same crucible in which the material is melted, but more often the melt is transferred into another crucible–mould<sup>89,99,102,106,114,128,130</sup> or into a ring placed on a smooth plate.<sup>104</sup> The crucibles and moulds used were made of platinum,<sup>90,97,101,115,126,127</sup> platinum–gold alloy,<sup>89,91,96,99,100,102,124</sup> platinum–gold–rhodium alloy,<sup>9</sup> some other materials, such as duralumin,<sup>106</sup> steel,<sup>104</sup> graphite<sup>93,106</sup> and glassy carbon.<sup>102,106,114,115,126,128,133</sup> The use of new platinum crucibles<sup>127</sup> or sputtering of the crucible walls with  $\text{CBrF}_3$ <sup>90</sup> is recommended to reduce adhesion. However, it is very difficult to avoid completely adhesion of the ingot to the metal crucible walls and to obtain specimens with smooth working surfaces.

The best results are attained when glassy carbon is used as a crucible and mould material; it is cheaper than precious metals, does not interact with metal oxides and makes it possible to obtain ingots having ideally smooth surfaces. Unfortunately, this material is subject to oxidation by air oxygen at high temperatures,

Table 2. Preparation of glassy specimens for XRFA using lithium metaphosphate<sup>125,128</sup> by fusion

Substance	Flux	Substance : flux ratio	Temperature (°C)
$\text{YBa}_2\text{Cu}_3\text{O}_x$	$\text{LiPO}_3$	1 : 2	780
$\text{Bi}_{0.7}\text{Pb}_{0.3}\text{SrCaCu}_2\text{O}_x$	90% $\text{LiPO}_3$ 10% $\text{Li}_2\text{CO}_3$	1 : 2	850
$\text{LiNbO}_3$	$\text{LiPO}_3$	1 : 3	800
$\text{CdWO}_4$	$\text{LiPO}_3$	1 : 10	850
$\alpha\text{-Al}_2\text{O}_3$	90% $\text{LiPO}_3$ 10% $\text{Li}_2\text{CO}_3$	1 : 10	900
$\gamma\text{-Al}_2\text{O}_3$	$\text{LiPO}_3$	1 : 20	850
$\text{SrTiO}_3$	90% $\text{LiPO}_3$ 10% $\text{Li}_2\text{CO}_3$	1 : 10	900
$\text{La}_3\text{Ga}_5\text{SiO}_{14}$	80% $\text{LiPO}_3$ 20% $\text{Li}_2\text{CO}_3$	1 : 20	950
$\text{La}_2\text{O}_3$	90% $\text{LiPO}_3$ 10% $\text{Li}_2\text{CO}_3$	1 : 25	950
$\text{Gd}_2\text{SiO}_5$	90% $\text{LiPO}_3$ 10% $\text{Li}_2\text{CO}_3$	1 : 30	950
$\text{SiO}_2$	70% $\text{LiPO}_3$ 30% $\text{Li}_2\text{CO}_3$	1 : 30	900
$\text{Ta}_2\text{O}_3$	70% $\text{LiPO}_3$ 30% $\text{Li}_2\text{CO}_3$	1 : 40	900
$\text{SrTiO}_3$	80% $\text{LiPO}_3$ 20% $\text{Li}_2\text{CO}_3$	1 : 10	900
$\text{ZrO}_2$	80% $\text{LiPO}_3$ 20% $\text{Li}_2\text{CO}_3$	1 : 10	900

and therefore fusion must be performed in an inert or reducing atmosphere which can be produced, in particular, by slow burning of graphite pieces placed in the furnace close to the crucible.<sup>125,128</sup> In one study,<sup>115</sup> the materials to be analysed were fused in a crucible made from glassy carbon placed in a container with a graphite cover. In the same work, the centrifugal technique was used to form a flat surface of the melt poured into a glassy carbon crucible. A similar procedure was also used in research.<sup>116</sup> It is much easier, however, to use as the working surface of a specimen the material obtained by the melt contacting the flat surface of the crucible.<sup>128</sup> Crucible-moulds made from glassy carbon are used at relatively low temperatures so they last a long time.

### NON-DESTRUCTIVE XRFA OF SOLID SAMPLES

If the samples to be analysed are homogeneous and have a regular shape and the calibration of the spectrometer is done correctly, then XRFA can be used to analyse the specimen without any preliminary destruction.

Such a technique has been used to analyse metal and alloy discs.<sup>55,134–136</sup> Non-destructive methods of analysis of functional materials,<sup>114,137,138</sup> natural pearls<sup>139</sup> and jewellery<sup>140</sup> have also been described. In the last case, accurate analysis is difficult because of differences in the size and shape of jewellery. Non-destructive analysis techniques for some materials are listed in Table 3. It is noteworthy that the non-destructive procedures developed for tungstates<sup>138</sup> ensure  $S_r$  values close to those defined by counting statistics of x-ray photons.

### DIRECT XRFA OF SOLUTIONS

This technique<sup>2</sup> is used only to determine elements which have characteristic emission lines that can penetrate the Mylar window of the specimen holder. Most liquids cannot be run under a vacuum. Bubbles released from solutions due to inadequate cuvette filling and

heating of the solution cause problems. Bubbles are particularly troublesome when the excitation source (tube) is located above the cuvette. Furthermore, it is difficult to maintain a constant distance between the surface of the sample liquid and the x-ray tube anode. Optics which have the source (anode of the tube) below the specimen are preferred for liquids. However, the expansion of the Mylar film of the cuvette also changes the anode-specimen distance and causes errors. A special cuvette design has been described which eliminates the error caused by uneven film tension.<sup>141</sup> In general, the direct analysis of liquids demands a certain skill from operators.

Direct analysis of liquids has been used in a number of recent studies. In particular, the determination of sulphates (after precipitation as  $\text{BaSO}_4$ ) through an excess of the precipitant ion  $\text{Ba}^{2+}$  in solution has been described.<sup>142</sup> The main components of Nd-Fe-B magnetic materials were determined after dissolution,<sup>143</sup> zinc in solution obtained by the ammonia leaching of ores,<sup>144</sup> uranium and thorium in Thorex process solutions,<sup>145</sup> zirconium in industrial solutions<sup>146</sup> and strontium in liquid nuclear wastes models.<sup>147</sup> Two procedures for the direct XRFA of solutions were described for high- $T_c$  superconducting (HTSC) materials. Yttrium, barium and copper contents were measured in superconducting yttrium-barium cuprate<sup>148</sup> after sample dissolution in hydrochloric acid ( $S_r = 5 \times 10^{-3}$ – $7 \times 10^{-3}$ ). Total and ionic silver in a YBaCuO-Ag superconducting composite were determined<sup>149</sup> after transfer into a solution containing nitric and acetic acids ( $S_r = 4 \times 10^{-2}$ ).

Direct solution analysis procedures are often calibrated using the internal standard method; nickel,<sup>143</sup> yttrium<sup>145</sup> and niobium<sup>146</sup> ions have been used as internal standards.

It should be noted that in liquid analyses errors are, as a rule, higher than those using glass-like specimens.

### USE OF QUASI-SOLID SPECIMENS

Since solid specimens are more favourable than liquid specimens for XRFA, some workers have proposed

Table 3. Characteristics of non-destructive XRFA methods

Material, Reference	Element to be determined	Concentration	$S_r$ , %	Reference materials	Calibration method
Plastic scintillator (organic glass) <sup>137</sup>	Gd	2–1000 ppm	$2 \times 10^{-2}$	Synthetic	Calibration graph construction
$\text{CdWO}_4$ <sup>138</sup>	Cd	26–36%	$9 \times 10^{-4}$	Part of the crystal (its neighbouring parts are analysed after destruction)	Theoretical correction methods
$\text{PbWO}_4$ <sup>138</sup>	W	46–56%	$7 \times 10^{-4}$		
	Pb	40–50%	$7 \times 10^{-4}$		
$\text{NaBi}(\text{WO}_4)_2$ <sup>138</sup>	W	37–45%	$6 \times 10^{-4}$		
	Bi	24–33%	$6 \times 10^{-4}$		
$\text{Al}_2\text{O}_3:\text{Ti}$ <sup>114</sup>	W	46–54%	$4 \times 10^{-4}$	A sample to be analysed	Internal standard, standard – background
Brass, bronze <sup>135</sup>	Ti	50–400 ppm	$2 \times 10^{-1}$		
	Cu, Pb, Fe, Ni, Sn, Mn, Zn	Chief elements, impurities	from $1 \times 10^{-3}$ to $5 \times 10^{-2}$		

<sup>a</sup> Relative standard deviation; systematic errors are negligible.

transforming liquids into quasi-solid bodies by increasing their viscosity by using additives<sup>150–154</sup> or by freezing them.<sup>151</sup> Methods have also been described which produce specimens of powders, chips, suspensions or liquids encapsulated in a low-melting organic matrix.<sup>155,156</sup>

Alkaline solutions were transformed into the quasi-solid state by adding a mixture of amylopectin and ethylene glycol.<sup>150</sup> The aliphatic hydrocarbon eicosane, when added to fuel oil, gives a homogeneous mass which is solid at room temperature.<sup>151</sup>

The introduction of gelatinizing substances, e.g. gelatine or agar, into solutions under study produced quasi-solid specimens of the desired size and shape suitable for different x-ray spectrometers.<sup>152</sup> To this end, 10% (by mass) of gelatine or 3% (by mass) of agar were added, in powdered form, to the solution to be analysed and left to stand and expand. The mixture was then heated to obtain a homogeneous solution. The hot solution was transferred into a cuvette made of Teflon and shaped corresponding to the spectrometer cuvette holder, where it was left until stiffening began; the cuvette was then turned upside down on to a smooth plate covered by Teflon film. As a result of the contact with the hydrophobic surface, an elastic gelatinous specimen was formed with a polished surface satisfactory for XRFA. Such a specimen can be obtained from aqueous solutions having a pH of 1–10, and also from organo-aqueous solutions containing ethanol, methanol or acetone. External standard, internal standard and background standard methods are suitable for con-

structing calibration graphs. Characteristics of the procedures developed are presented in Table 4. The first three of the procedures listed are for direct water analysis; HTSC ceramics was decomposed in acid; to determine toxic impurities in drinking water at the minimum permissible concentration level, they were extracted as diethyldithiocarbamates and then re-extracted into the aqueous phase by means of exchange reactions with mercury(II) ions.

To prepare specimens from organic solutions, in particular from organic extracts which are concentrates of analyte elements, a procedure of organogel formation using gelatine has been proposed.<sup>153</sup> Aqueous gelatine and surfactant solutions were added to the extract in small amounts and the mixture, thoroughly mixed, was left until gelation began. The specimen surface was formed by contacting the mixture obtained with a Teflon film placed on a plate with a smooth surface. This technique was used to determine Cu, Zn and Ni by XRFA in aqueous solutions after concentration by extraction ( $S_r = 0.1$ ).

In cases when only a small volume of an aqueous solution is available for analysis, a procedure<sup>154</sup> allowing one to obtain an organic glassy polymeric specimen from sucrose is suitable. A 1 g amount of sucrose was added to 2–3 cm<sup>3</sup> of solution and mixture was heated at 250–300 °C for 3–5 min. Under these conditions, sucrose inversion followed by its caramelization took place while the water added evaporated completely. The specimen was formed by cooling of the mass obtained on the smooth surface of a Teflon plate or film in a

**Table 4. Characteristics of methods developed for XRFA using quasi-solid specimens (Spark-1 spectrometer)<sup>152–154</sup>**

Sample analysed; gelatinizing substance	Element to be determined	Calibration method	Concentration	$S_r$ , <sup>a</sup>
Solutions after copper board etching;	Cu	External standard	2.5–40 g l <sup>-1</sup>	0.08
gelatine		Standard – background	1–10 g l <sup>-1</sup>	0.09
Waste from ZnSe production;	Se	Internal standard Ga	0.4–1 g l <sup>-1</sup>	0.1
gelatine		Internal standard As	0.2–2 g l <sup>-1</sup>	0.06
		Standard – background	0.2–2 g l <sup>-1</sup>	0.05
Waste from GaAs production gelatine	Ga	Standard – background	0.4–3 g l <sup>-1</sup>	0.06
HTSC ceramics; gelatine	Y	Standard – background	4.5–18.5%	0.04
	Ba		31.2–51.7%	0.06
	Cu		16.8–47.5%	0.04
	Y	External standard	4.5–18.5%	0.04
	Ba		31.2–51.7%	0.05
	Cu		16.8–47.5%	0.03
Drinking water; gelatine	Cu, Pb, Bi, Zn, Fe, Ni	External standard	0.1–1 mg l <sup>-1</sup>	0.01–0.1
Waste after crystallization	Cu	External standard	1 mg l <sup>-1</sup>	0.07
concentration; sucrose	Se		0.1 mg l <sup>-1</sup>	0.09

<sup>a</sup> Relative standard deviation; systematic errors are negligible.

mould made of Teflon or another hydrophobic material. The specimen mass is 2–3 times smaller than that of the initial solution, that is, the specimen preparation procedure itself causes the concentration of the elements to be determined.

## PREPARATION OF THIN SPECIMENS

In a number of laboratories, thin specimens are used. In the limiting case the specimen thickness is so small that the absorption of primary and secondary emission in it may be neglected. In this case, chemical composition does not influence the intensity of the analytical line, and a direct, strictly linear dependence must be observed between the intensity of the analytical lines and element concentrations in the specimen. However, not many specimens correspond to the criterion of 'thin' layer, and often it is necessary to work under the conditions of an 'unsaturated' layer, when the specimen thickness is to be strictly fixed. Since the analytical signal is obtained from a small amount of substance, this type of analysis allows one to determine only relatively high element concentrations (e.g. in analytical concentrates).

Volkov *et al.*<sup>157</sup> prepared a carboxymethylcellulose (CMC) solution in the water sample to be analysed, poured it into a ring placed on a polyethylene substrate and dried it. The CMC film separated easily from the substrate together with the ring was used as a specimen. A procedure has been described<sup>158</sup> for obtaining thin-film samples of Cu–Ag and Cu–Mn alloys by condensation in a vacuum of  $10^{-3}$  Pa on to a polymeric substrate. It should be noted that the validity of this method depends heavily on the coincidence between the compositions of the film sputtered and of the alloy to be analysed. To analyse domestic dust<sup>159</sup> it was applied to a sticky tape consisting of paper and polyester. Copper and zinc were determined in a catalyst<sup>160</sup> by applying about 2 mg of the powder to Cellophane film covered with a glue. Powder of coals, fly ash and other substances were ground, suspended in cyclohexane, filtered through a Nuclepore filter and covered with poly(vinyl acetate) film.<sup>161</sup>

The total reflection method (TRXRF) reported more than 20 years ago allows the analysis of thin samples and lowers the element's detection limits by 2–3 orders of magnitude, since the main background component, namely the incident primary excitation radiation and scattered radiation, undergoes essentially total reflection on the smooth sample surface and does not reach the detector. Recent achievements in the field of TRXRF were considered in a review.<sup>162</sup> Optically smooth plates of quartz, glass, silicon<sup>163</sup> and some other materials are used as substrates. When a liquid sample is to be analysed, several mm<sup>3</sup> of the sample are applied to the substrate and dried.<sup>164–169</sup> This technique was used to analyse water,<sup>167,168</sup> titanium dioxide (rutile) transferred into solution,<sup>165</sup> analytical concentrates<sup>166,168</sup> and aerosols after their transfer into solution<sup>169</sup> and for the determination of a number of light elements.<sup>170</sup> In the analysis of aerosols, Schneider<sup>171</sup> separated them by particle size and trapped them on quartz plates using a

cascade impactor. A sample of paint having a mass of several micrograms was scraped off the surface of a car and spread on a quartz substrate.<sup>172</sup> From biological objects, thin (10–20  $\mu\text{m}$ ) sections of frozen tissues were obtained by a microtome and applied to and smoothed out on quartz plates.<sup>173</sup> The detection limits of elements by this method are 1–10  $\text{pg cm}^{-3}$  in solution, about 10  $\text{ng cm}^{-3}$  in biological objects and  $10^{-3}$  ppm by mass in high-purity metals after matrix separation.<sup>166</sup> Owing to the small incidence angle of primary x-rays, this method was used when determining the element composition of surface layers for massive silicon<sup>174</sup> and gallium arsenide<sup>175</sup> samples. In the latter case, the variation of the incidence angle allowed the change in the content of iron impurity in the depth of the specimen to be determined.

## PRECONCENTRATION OF IMPURITIES

Since the XRFA detection limits for elements are relatively high, their preliminary concentration from solutions or gaseous phases to obtain a solid sample (most suitable for the preparation of a specimen for x-ray measurements) is a procedure that is widely used. A simple way is to evaporate solutions applied to a solid substrate or paper filter.

To determine metal impurities (Y, Cr, Fe, Ni, Cu, Zn, Nb) in crude oil, the sample (1.5 cm<sup>3</sup>) was evaporated under an IR lamp on a Mylar substrate and the dry residue obtained was subjected to analysis.<sup>176</sup> Lichen samples were decomposed by heating with HNO<sub>3</sub>–HF mixture in a Teflon autoclave, and a fraction of the solution obtained was placed on a Mylar film and evaporated under vacuum.<sup>177</sup> Blood samples were dried on the surface of Mylar film at 4–6 °C.<sup>178</sup> To determine a series of elements in biological objects and liquids, the samples were diluted with water or ground in a mortar, then a sample of 5–10 mm<sup>3</sup> was applied to a polymeric film and dried at room temperature.<sup>179</sup> Special devices for fast solvent evaporation have been proposed.<sup>180,181</sup> In another method, an aqueous solution or organic extract was evaporated on to a Teflon plate having a spherical hollow (Fig. 4).<sup>181–183</sup> If an organic extract containing mainly light elements is evaporated on to such a plate, the specimen obtained meets the criterion of 'thin.' Leaves were dried by freezing, then placed

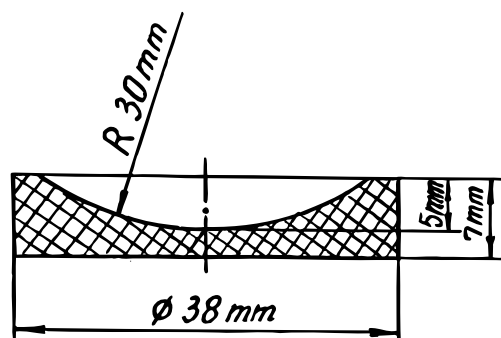


Figure 4. Teflon plate with a hollow for evaporation of solutions before XRFA.<sup>181</sup>

between two Mylar films and attached to an aluminium sample holder by means of vacuum grease.<sup>184</sup> In many laboratories,<sup>185–192</sup> small amounts of liquid samples were applied to paper filters and dried, and the filters so prepared were used as specimens. Using this technique, gold was determined in geological samples of complicated composition after its extraction as  $\text{HAuCl}_4$  by dimethyl ketone,<sup>185</sup> 11 elements in human blood,<sup>188</sup> Cu, Ni, Co, Fe and Cr in heat-resistant alloys,<sup>190</sup> elements contained in processing solutions of zeolite production<sup>191</sup> and fission products in spent nuclear fuel.<sup>192</sup>

Placing a solution on a filter paper is a relatively simple procedure, although its applications are limited since the results obtained frequently contain significant errors. The efficiency of the concentration technique can be enhanced by using a repeated application and drying procedure. Specimens so obtained may be inhomogeneous owing to the 'chromatographic effect'.<sup>2</sup> Although the filter is fixed, in one way or another, on a holder shaped as a ring or hollow cylinder,<sup>185,187,191</sup> it is impossible to avoid completely warping of the filter during the course of drying.

Solid particles of disperse systems (aerosols or suspensions) are concentrated by filtration through nuclear or fibrous filters.<sup>193–197</sup> To determine lead in atmospheric air,<sup>196</sup> the latter was pumped for 24 h at a rate of  $1.1\text{--}1.7\text{ m}^3\text{ min}^{-1}$  through a fibre-glass filter and then exposed for 24 h at a specified temperature and humidity and analysed using a standard additions method.

After the concentration of an aerosol containing Mg, Al, Si, K, Ca, Ti, Mo, Fe, Zn, Cu and Pb on a fibrous filter, the latter was compacted in an acrylic mould under  $10^7$  Pa pressure, resulting in a solid specimen convenient to use and stable for a long time.<sup>195</sup>

Precipitation or coprecipitation from solutions is widely used to concentrate elements before determining them by XRFA. Rare earth elements (REE) were coprecipitated as poorly soluble fluorides with yttrium fluoride when determining them in steel.<sup>198</sup> REE hydroxides were coprecipitated on  $\text{Fe}(\text{OH})_3$ .<sup>199</sup> The same collector was used to coprecipitate manganese when determining it in alloyed steel<sup>200</sup> and for coprecipitation of phosphates as iron(III) phosphate in waste water analysis.<sup>201,202</sup> In the last study,<sup>202</sup> precipitation was performed in the presence of activated charcoal. When determining Co, Ni and Fe in titanium alloys, these elements were coprecipitated with  $\text{In}(\text{OH})_3$ .<sup>203</sup> After separation of tantalum using extraction chromatography, impurities contained in the technical tantalum were coprecipitated with indium(III) oxinate in the presence of tannin.<sup>204</sup>  $\text{Zr}(\text{OH})_4$  was used as a collector to coprecipitate hydroxides of Sb, Sn, Bi, Pb, As and Fe.<sup>205</sup> To analyse blood serum<sup>206</sup> and natural waters,<sup>207</sup> selenium was coprecipitated with iron, cadmium or cobalt pyrrolidinedithiocarbamate and the suspension obtained was filtered through a Millipore membrane filter. When determining heavy metals in natural waters, complexes with 8-mercaptoquinoline were coprecipitated using 8-quinolyl sulphide as a collector.<sup>208</sup> Metal impurities in biological objects were complexed with 1-(2-pyridylazo)-2-naphthol and coprecipitated on the excess of reagent.<sup>209</sup>

Phosphate and arsenate ions were separated from aqueous solutions as poorly soluble quinidinium phosphoro- and arsenomolybdate.<sup>210</sup> To determine bromides in sea water and processing solutions, those were precipitated as  $\text{AgBr}$ .<sup>211</sup>

In addition to paper filters, membrane,<sup>203,205,206,211</sup> nuclear (Nuclepore)<sup>208</sup> and glass filters<sup>210</sup> have been used to collect precipitates from solutions. The concentrates obtained were separated from the filters and compacted<sup>199,200,208,209</sup> or placed between two Mylar films in a special holder.<sup>202</sup> In other works, a membrane filter together with the precipitate was pressed between two polyethylene terephthalate films,<sup>203</sup> or the filter with precipitate was dried and covered with a polymer film.<sup>206</sup> In some cases,<sup>198,204,205</sup> an element in the collector was used as the internal standard for calibration.

Concentration by means of precipitation or coprecipitation can be used to analyse many different materials, but this procedure is labour consuming and difficult to automate. Analytical procedures including cake compaction together with the filter seem preferable, since in these cases smooth-surfaced specimens are obtained.

Many studies have dealt with adsorption/absorption concentration of elements prior to XRFA measurements. This method was used mainly to analyse waters [determinations of  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{SiO}_3^{2-}$  and  $\text{SO}_4^{2-}$ ,<sup>212</sup> Mo, W, V, Cr and As,<sup>213</sup> heavy metals,<sup>214–217</sup> As(III) and As(V),<sup>218,219</sup> Pb,<sup>220</sup> Ag and Hg<sup>221,222</sup> and U and Cr<sup>223</sup>]. Adsorption concentration was also used when analysing mineral raw materials (determination of REE,<sup>224,225</sup> platinum group metals,<sup>226</sup> gold and silver,<sup>227</sup> gold and platinum,<sup>228</sup> gold<sup>229</sup> and to determine REE in petrochemical products,<sup>222</sup> some metals in metallic lithium<sup>230</sup> and silver and gold in non-ferrous metallurgy products.<sup>231</sup>

If a solid material is to be analysed, it is transferred into solution prior to concentration by adsorption. Among the most often used adsorbents are those containing immobilized complexing reagents: polyacrylonitrile modified by polyethylene polyamine,<sup>212,213</sup> naphthalene modified by 1-(2-pyridylazo)-2-naphthol,<sup>232</sup> aminostyrene-divinylbenzene copolymer with grafted hydroxyaminodiacetic acid,<sup>224</sup> azothiozane-2,4-dithiol immobilized on polystyrene,<sup>227</sup> cellulose with grafted amino,<sup>218</sup> mercapto<sup>219</sup> or aminocarboxy<sup>215</sup> groups, *N*-vinylpyrrolidone copolymer with ethylene glycol vinyl glycidyl ether modified by thiourea,<sup>221,231</sup> polyurethane foam impregnated with 1-(2-pyridylazo)-2-naphthol<sup>214</sup> and some commercially available chelating adsorbents, e.g. Poliorgs.<sup>226,228,233</sup> In many cases, ion-exchange membranes have been used for the pre-concentration of impurities.<sup>220,222,223,230</sup>

In a number of cases, the elements to be determined were complexed with organic reagents introduced into the sample solution, and then concentrated using a non-selective adsorbent. When determining Cu, Co, Ni, Fe, Zn, Pb, Cd, Mn, Hg and Bi in water, their complexes with 1-(2-pyridylazo)-2-naphthol were first obtained and then adsorbed on an acetylcellulose filter of the Vladipor type.<sup>216</sup> Activated charcoal was used to adsorb REE complexes with 8-hydroxyquinoline<sup>225</sup> and that of gold with thiourea.<sup>229</sup> The use of unsaturated tungsten-phosphorus compounds as adsorbents for a



series of transition metals has been proposed;<sup>217</sup> in such a case, these compounds act as macroligands.

When using finely dispersed adsorbents, the process was performed mainly in the static mode.<sup>212,217,221,225–229,231,232</sup> The same mode was used for adsorbents shaped as tablets,<sup>223</sup> discs<sup>214</sup> or fibrous textiles.<sup>212</sup> Adsorption on filters (membranes) in the dynamic mode<sup>215,218–220,233</sup> using a peristaltic pump was found to be very effective, since, in such cases, the adsorbent capacity is used to the maximum extent and the process runs in an automatic regime and is less time consuming. Preconcentration on a column<sup>230</sup> appears to be less effective in this case.

Filters (membranes) with elements to be determined have been used as specimens;<sup>212,215,216,218,220,227,229,233</sup> after adsorption/absorption, the filters were dried and fixed to Mylar film or to a rigid support. It has also been proposed<sup>221,228,231</sup> to collect a finely dispersed adsorbent on a paper filter; the concentrate obtained is then fixed on the filter with aerosol varnish<sup>221,231</sup> or mixed with polystyrene and poured into a cuvette for powders.<sup>228</sup> In some studies,<sup>224,226,227,232</sup> the concentrates obtained were compacted, sometimes with the addition of a binder, e.g. boric acid<sup>226</sup> or cellulose.<sup>224</sup> The use of a compacted specimen allowed<sup>227</sup> the detection limits for the elements to be determined to be lowered substantially, and enhanced by an order of magnitude the reproducibility compared with uncompact concentrates. Concentrates based on an organic adsorbent were wetted with alcohol, charred and then mixed with polystyrene and pressed.<sup>212,213</sup> In other work<sup>107</sup> the analyte elements were adsorbed on zeolites, and then converted into glassy specimens by means of fusion with  $\text{Li}_2\text{B}_4\text{O}_7\text{—LiBO}_2$ .

A relatively seldom used method is to elute the elements after adsorption/absorption preconcentration on a column. The eluate was evaporated on an aluminium disk.<sup>230</sup>

An original technique was proposed<sup>217</sup> for producing a specimen after the adsorption preconcentration. The finely dispersed concentrate was mixed with an epoxy resin and the half-liquid mixture obtained was applied to a disk made from polycarbonate and left to spread over the disk surface uniformly prior to hardening.

The wide use of adsorption/absorption preconcentration is explained by the fact that this method allows one to obtain a solid concentrate suitable for direct application in XRFA. The results seem to be the best when preconcentration is performed in the dynamic mode on a filter (membrane) using a peristaltic pump.

A considerable number of papers have been dedicated to XRFA with preliminary extraction concentration of the elements to be determined. These papers can be subdivided by convention into two groups. Many workers used the customary liquid extraction of the analyte elements or the main material components as various complex compounds, and then specimens were obtained by the evaporation of an organic solvent or aqueous phase on a suitable solid support.<sup>181,182,204,234–238</sup> In the other group,<sup>239–250</sup> the elements to be determined were extracted from solution by means of low-melting organic compounds which solidify at room temperature,

so that the extracts obtained can be used immediately as XRFA specimens.

Liquid extraction as a preliminary concentration method was used to determine gold in ores,<sup>185</sup> minor elements in metallic tantalum,<sup>204</sup> bismuth in lead concentrates,<sup>234</sup> silver in copper ones,<sup>235</sup> selenium in animal tissues,<sup>236</sup> niobium and tantalum<sup>237</sup> and molybdenum and tungsten<sup>238</sup> in rocks, thallium in NaI(Tl) scintillation single crystals<sup>182</sup> and REE in doped calcium fluoride single crystals.<sup>181</sup>

In one study,<sup>204</sup> the main component, tantalum, was separated by extraction chromatography on a column filled with Teflon impregnated with tributyl phosphate. In a series of papers, the concentration of minor amounts of elements is described. Thus, gold was extracted with methyl isobutyl ketone as  $\text{HAuCl}_4$ ,<sup>185</sup> Nb, Ta, Mo and W, as complexes with benzoylphenylhydroxylamine, toluene being the extractant,<sup>237,238</sup> bismuth, in the form of the diethyldithiocarbamate complex,<sup>234</sup> silver, as the dithizonate (with chloroform)<sup>235</sup> and REE, as complexes with morin (20% tributyl phosphate solution in isoamyl alcohol was used as the solvent).<sup>181</sup> Thallium was extracted selectively with chloroform as the complex with an azamacrocyclic, an analogue of dibenzo-18-crown-6, in the presence of dipicrylamine ion.<sup>182</sup> Selenium was extracted in the presence of 2,3-diaminonaphthalene with chloroform.<sup>236</sup>

To prepare a specimen, the concentrate was evaporated on a Teflon substrate<sup>181,182</sup> (Fig. 4) or on filter-paper.<sup>204</sup> A polymer referred to as Chlorin was added to the organic concentrate and the solution was then applied onto a Mylar substrate and evaporated.<sup>234,235</sup> A thin polymer film was obtained. In some cases,<sup>237,238</sup> cellulose powder was added to the extract and, after the solvent had been evaporated, the residue was pressed into a tablet.

When determining selenium, it was reduced in the organic phase to the element by means of hydroxylamine and the precipitate was then transferred on to a filter.<sup>236</sup> The preparation of a gel-like specimen from the organic extract was shown to be possible<sup>153</sup> by the addition of a surfactant and aqueous gelatine solution.

The use of low-melting extractants has been described for the determination of small amounts of Au,<sup>239</sup> Cu, Zn, Cd and Pd,<sup>240</sup> Ti,<sup>241</sup> Ga and In,<sup>243</sup> Sc,<sup>244</sup> metal impurities,<sup>247</sup> Cd, Bi, Pb, Cu, Se, Y, Sr and Zr<sup>249</sup> in natural and industrial waters, V in environmental objects,<sup>242</sup> Bi, Se and Te in ores and minerals,<sup>248</sup> Al in non-ferrous alloys<sup>245</sup> and Pt and Pd in various objects.<sup>250</sup>

Low-melting extractants that have been used include  $\text{C}_{17}\text{—C}_{20}$  aliphatic monocarboxylic acids<sup>239,248</sup> and their mixtures with various organic reagents, such as 2,2'-dipyridyl or 1,10-phenanthroline,<sup>240</sup> trialkylamine,<sup>241</sup> di-2-ethylhexylphosphoric acid (DEHPA),<sup>244,245</sup> DEHPA with tributyl phosphate (TBP),<sup>243</sup> DEHPA with TBP and amines<sup>249</sup> and dioctyl sulphide or trioctylphosphine oxide.<sup>250</sup>  $\text{C}_{16}\text{—C}_{21}$  long-chain alcohols with admixtures of various reagents (DEHPA, TBP and amines<sup>249</sup> and 1-(2-pyridylazo)-2-naphthol<sup>245</sup>) serve also as low-melting extractants.

Vanadium was extracted from the substance under study with molten 8-hydroxyquinoline-palmitic acid

mixture in an analytical autoclave.<sup>242</sup> When determining small amounts of gold, the 'double concentration' technique was used, i.e. a combination of extraction with low-melting aliphatic acids and coprecipitation.<sup>239</sup>

In most cases, the extraction with low-melting organic substances was performed by shaking a retort containing the solution under study and the extractant in a water-bath. The extract solidified at room temperature and was then removed from the retort, remelted and a specimen was formed in a Teflon or metal ring placed on a smooth surface.

When combining XRFA with extraction concentration, the use of low-melting organic substances or the evaporation of the liquid organic extract on a Teflon substrate having a recess shaped as a spherical segment seem to be the most suitable technique.

Free CuO in a superconductor based on yttrium-barium cuprate was determined<sup>251</sup> ( $S_r = 0.12$ ) after the selective dissolution of the base and other minor phases in acetic acid and transfer of the residue into solution by means of hydrochloric acid; the concentrate was evaporated on the Teflon substrate (Fig. 4) and was fixed with aerosol varnish.

An original method was described<sup>252</sup> that included the electrochemical concentration of microgram amounts of V, Cr, Mn, Co, As, Bi and Sr in aqueous solutions with subsequent XRFA of the concentrates obtained. In that work, electrodeposition of the elements mentioned was performed on graphite substrates.

It has been proposed<sup>183,253</sup> to combine the XRFA determination of impurities in pure salts with preliminary crystallization concentration. The concentration method is based on the displacement of impurities towards the melt (or solution) during the directional crystallization of the substance under study and is characterized by universality with respect to impurities of various types.<sup>254</sup> The low-temperatures directional crystallization of water-salt eutectics was used to determine bromides in CsI<sup>183</sup> and heavy metals in CsI, RbNO<sub>3</sub> and KNO<sub>3</sub>.<sup>253</sup> Isolating the ingot part crystallized in the last stage, an analytical concentrate was obtained as a small volume of the salt aqueous solution. The concentrate was evaporated on a Teflon substrate.<sup>183</sup> This concentrate did not meet the 'thin-layer' criterion and had a 'coarse-grain powder' structure. Nevertheless, a procedure having satisfactory metrological characteristics was developed for that case also (when calculating the analysis results, the mass of the macrocomponent salt in the concentrate was taken into account). Dry gelatine was added to the concentrates produced by low-temperature directional crystallization of aqueous salt solutions;<sup>253</sup> by this method, quasi-solid gel-like specimens were prepared (see above).

Cu and Se in concentrations as low as 1 and 0.1 mg dm<sup>-3</sup>, respectively, could be determined in water and processing solutions after low-temperature directional crystallization of the water under study.<sup>154</sup> To the concentrate obtained, sucrose was added to prepare a polymeric glassy disk, as described in the section Use of Quasi-Solid specimens.

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## CONCLUSION

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It is well known that specimen preparation is the source of the largest errors of XRFA. Our work and those of others reported in recent publications bear this out.

Most of the specimen preparation methods in use nowadays were developed long ago. However, some new efficient variations of these methods and new techniques widening the possibilities of XRFA have recently been proposed.

The simplest yet least accurate method of XRFA is the direct analyses of powders, in particular heterogeneous powders. The use of pressed powders gives more accurate results. However, here, as in the first-mentioned case, large errors are possible owing to differences in the granulometric and phase compositions of the substance under analysis and the reference materials. These errors can be minimized to a certain extent by pressing powders to a constant volume.

Fused glass-like specimens are widely used for precise analyses, including the determination of major components of materials of complex composition. Fusion of oxide materials with lithium metaphosphate flux using glassy carbon crucibles as moulds has been found to be a useful technique.

The non-destructive analysis of solid samples imposes a series of strict requirements with respect to their chemical resistance, size, surface state and demands to solve the problem of calibration. This variant of XRFA method has been shown to be suitable not only for metals, but also for a series of oxide single crystals.

Direct analysis of solutions is used fairly often, but this demands a certain skill from operators. Difficulties arising in direct solution analysis can be avoided by using various approaches which increase the liquid viscosity to make a quasi-solid specimen.

Analysis by the TRXRF method allows the detection limit to be lowered by 2–3 orders of magnitude in comparison with conventional XRFA in thin layers. However, this mode is not very widely used outside the semiconductor business owing to the high equipment cost.

Direct XRFA is characterized by relatively high detection limits, and therefore nowadays the method is often combined with preconcentration of the analyte elements from solutions or gaseous phases. For this purpose various methods are in use, including solution evaporation, suspension or aerosol filtration (when analysing the solid particles of a disperse system), precipitation, coprecipitation, adsorption/absorption or extraction of the elements to be determined from solutions, electrochemical deposition of elements and directional crystallization of water and solutions. Sometimes selective dissolution of some phases of hard materials is used. Among the methods listed, membrane adsorption in the dynamic mode using a peristaltic pump, extraction with low-melting organic substances and low-temperature crystallization as preconcentration techniques are worthy of note.

## REFERENCES

1. S. Uhlig and M. Peters, *Analisis* **20**, No. 8, 48 (1992).
2. A. N. Smagunova and Y. N. Bazykina, *Zh. Anal. Khim.* **40**, 773 (1985).
3. R. van Grieken, *Anal. Chim. Acta* **143**, 3 (1982).
4. A. N. Smagunova, T. N. Gunicheva, O. M. Karpukova and V. A. Kozlov, *Zavod. Lab.* **59**, No. 4, 20 (1993).
5. S. A. Volodin and A. G. Revenko, *Zh. Anal. Khim.* **44**, 1541 (1989).
6. A. L. Tsvetyansky and A. N. Yeritenko, *Zavod. Lab.* **56**, No. 4, 25 (1990).
7. A. N. Smagunova, O. F. Rozova and N. N. Skribko, *Zavod. Lab.* **56**, No. 9, 28 (1990).
8. K. H. Koch, K. Ohls and J. Flock, *Lab Pract.* **14**, 1022 (1990).
9. O. F. Rozova, I. M. Preklina, N. N. Skribko, A. V. Loran, N. V. Popova and A. N. Smagunova, *Zavod. Lab.* **62**, No. 6, 17 (1996).
10. V. P. Afonin, *Fresenius' Z. Anal. Chem.* **335**, 54 (1989).
11. A. J. Oliver and H. H. Bennett, *XRF Analysis of Ceramics, Minerals and Other Materials*. Wiley, New York (1992).
12. A. G. Revenko, *Zavod. Lab.* **60**, No. 11, 16 (1994).
13. F. I. Lobanov, *Zavod. Lab.* **47**, No. 10, 1 (1981).
14. *Chem. Br.* **27**, 798 (1991).
15. S. B. Torok and R. E. van Grieken, *Anal. Chem.* **64**, 180 (1992); **66**, 186 (1994).
16. P. Wobrauschek, H. Aiginger, G. Owesny and C. Streli, *J. Trace Microprobe Tech.* **6**, 295 (1988).
17. S. Torok, J. Labar, J. Injuk and R. Van Grieken, *Anal. Chem.* **68**, No. 12, 467R (1996).
18. H. Yuan, Y. Liu and L. Jia, *Fanxi Huaxue* **17**, 652 (1989).
19. T. S. Aisujeva, T. N. Gunicheva and A. L. Finkelshtein, *Zh. Anal. Khim.* **45**, 160 (1990).
20. V. J. Borkhodoev, *Zh. Anal. Khim.* **51**, 226 (1996).
21. J. Gyves, M. Baucells, G. Lacort and M. Aoura, in *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Abstracts*, p. 213, Atlanta, GA (1993).
22. J. Kierzek, B. Maloweska-Bucko, L. Wawrzonek and J. L. Parus, *J. Radional. Nucl. Chem. Art.* **158**, 401 (1992).
23. R. V. Reddy, G. Kalpana, V. J. Koshy, N. V. S. Apparao, M. C. Jain and R. V. Patel, *Analyst (London)* **116**, 847 (1991).
24. K. N. Belikov, A. B. Blank and N. I. Shevtsov, *Zh. Anal. Khim.* **52**, 872 (1997).
25. S. V. Kubarev and V. A. Tsarenko, in *International Conference on Noble and Rare Metals, Abstracts, Part 2*, p. 23, Donetsk (1994).
26. A. N. Smagunova, O. F. Rozova and S. B. Tarasenko, *Zavod. Lab.* **48**, No. 4, 25 (1982).
27. V. I. Karmanov, L. A. Shevchenko and V. V. Voroshilo, *Zavod. Lab.* **57**, No. 4, 26 (1991).
28. V. A. Shvetsov, V. P. Chicheva, T. V. Bashkirov and V. V. Pakhomova, *Zavod. Lab.* **57**, No. 11, 24 (1991).
29. V. V. Zagorodny, *Zh. Anal. Khim.* **47**, 1428 (1992).
30. N. M. Kochmola and K. I. Gorokhov, *Zh. Anal. Khim.* **45**, 80 (1990).
31. K. K. Nielson and V. C. Rogers, *Adv. X-Ray Anal.* **29**, 587 (1986).
32. B. I. Kitov, A. V. Smagunova and M. A. Portnov, *Zh. Anal. Khim.* **45**, 1927 (1990).
33. A. B. Blank, N. I. Shevtsov and I. I. Mirenskaya, *Zh. Anal. Khim.* **36**, 1272 (1981).
34. S. I. Duimakaev, M. G. Tarnopolsky, T. G. Duimakaeva and A. Y. Shpolyansky, *Zavod. Lab.* **59**, No. 11, 16 (1993).
35. M. Iwatsuki, J. Niino and T. Fukasawa, *Nippon Kaisui Gakkaishi* **45**, 294 (1991).
36. I. Gresits, S. tolyesi, L. G. Nagy and J. Solymosy, *J. Radioanal. Nucl. Chem. Lett.* **164**, 275 (1992).
37. C. T. Jap, S. M. Tang and S. Wongnawa, *Appl. Spectrosc.* **41**, 1335 (1987).
38. H. Li, C. He and X. Yuan, *Fanxi Huaxue* **18**, 549 (1990).
39. T. Gunicheva, T. Aisueva and V. Afonin, *X-Ray Spectrom.* **24**, 187 (1995).
40. M. Matherny and V. Balgava, *Fresenius' J. Anal. Chem.* **346**, 162 (1993).
41. A. G. Revenko, G. P. Petrova and V. M. Novikov, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 412, Moscow (1990).
42. Howard M. Kanare, in Report of 44th Denver X-Ray Conference Workshop on Specimen Preparation for XRF Analysis (1995).
43. G. Jing, S. Liu, G. Ji, K. Su, Y. Li and G. Xiao, *Changchun Dizhi Xueyuan Xuebao* **24**, 472 (1994).
44. T. Nobutaka and H. Toshiaki, *Iwate Digaku Kyoikuga-Kubu Kenkyu Nenpo* **55**, No. 1, 89 (1995).
45. S. Custo Graciela, V. de Leyt Dora and O. Guido Osvaldo, *Can J. Appl. Spectrosc.* **37**, 176 (1992).
46. G. Li and S. Fan, *J. Geochem. Explor.* **55**, No. 1-3, 75 (1995).
47. R. S. Sokhi, C. Gray, K. Gardiner and L. G. Earwaker, *Nucl. Instrum. Methods Phys. Res. B* **49**, 414 (1990).
48. T. Perez Ruiz, M. Hernandez Cordova and R. Ortiz-Gonzalez, *Microchem. J.* **39**, 220 (1989).
49. M.-T. Garcia-Gonzalez, M. P. Haro-Ruiz and A. Hernandez-Laguna, *Analyst (London)* **117**, 1169 (1992).
50. G. Radha Krishna, H. R. Ravindza, B. Gogalan and S. Syamsunder, *Anal. Chim. Acta* **309**, 333 (1995).
51. H. M. West, J. Cawley and R. Wills, *Analyst (London)* **120**, 1267 (1995).
52. A. G. Revenko, S. A. Volodin, E. I. Kuznetsova and L. I. Pazdnikova, *Zavod. Lab.* **54**, No. 12, 44 (1988).
53. A. M. Barouni, L. Bakos and E. Zemplén-Papp, *J. Radioanal. Nucl. Chem. Lett.* **128**, 423 (1988).
54. V. Lucia, R. Salvador and K. Imakuma, *Instituto de Pesquisa de Enezia Nuclear. Publicações (Brazil)*, No. 130, 1 (1988).
55. T. Sofilic and D. Maljkovic, *X-Ray Spectrom.* **18**, 25 (1989).
56. Y. Liu, Q. Fan and D. Li, *Adv. X-Ray Anal.* **30**, 309 (1987).
57. O. Zhai, *Bull. Geol. Surv. Can.* No. 451, 73 (1993).
58. M. Yoto, A. Ishii and P. Ishii, *Bunseki Kagaku* **36**, 842 (1987).
59. G. S. Lodha, K. I. S. Sawhney and V. M. Choubey, *X-Ray Spectrom.* **18**, 225 (1989).
60. M. Lal, R. K. Choudhury, D. Joseph, H. M. Bajpai and C. S. P. Iyer, *J. Radioanal. Nucl. Chem. Lett.* **137**, 127 (1989).
61. S. A. Bakulin, T. B. Shubina and T. V. Blestkina, Deposited Doc. No. 110-90khp, ONIITEKHIM, Cherkasy, Ukraine (1990); from *Ref. Zh., Khimiya* Abstr. 12G40 (1990).
62. N. S. Salakhutdinov, T. A. Privalova, A. P. Nikolsky, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 414, Moscow (1990).
63. G. Ma and G. Li, *X-Ray Spectrom.* **18**, 199 (1989).
64. P. Wilson, M. Cook, J. Cawley, L. Giles and M. West, *X-Ray Spectrom.* **24**, 103 (1995).
65. E. V. Savina, T. P. Mamulova, V. G. Kostin, T. P. Blaschuk and N. A. Belyaeva, *Zavod. Lab.* **57**, No. 10, 7 (1991).
66. M. Baucells, C. Lacort, M. Roura and J. de Gyves, *Analyst (London)* **113**, 1325 (1988).
67. T. K. Smith and M. N. Ingham, *Adv. X-Ray Anal.* **32**, 227 (1989).
68. V. J. Borkhodoev, *USSR Pat.* 4 254 997/31 (1990).
69. C. Boni, A. Caridi, E. Caredda, G. M. Braga Marazzan and P. Redaelli, *Nucl. Instrum. Methods Phys. Res. B* **49**, 106 (1990).
70. U. Meduna and H. P. Schafer, *Lab Pract.* **13**, 130 (1989).
71. F. A. Ali, Q. A. A. Jassim and N. H. Alrazak, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 338, Moscow (1990).
72. H. P. Longerich, *X-Ray Spectrom.* **24**, 123 (1995).
73. T. N. Khlopina and L. G. Kim, *USSR Pat.* 3 995 845/23-16 (1987).
74. N. S. Baimursina, N. N. Naumenko, E. G. Tarasova, R. A. Filippova, K. I. Chaly and B. S. Shokhov, *Zavod. Lab.* **58**, No. 2, 54 (1992).
75. V. N. Talanova and I. S. Smirnova, *Zavod. Lab.* **61**, No. 12, 21 (1995).
76. N. I. Shevtsov, I. I. Mirenskaya and N. B. Lebed', in *Production and Investigation of Optical and Scintillation Materials*, p. 149. Institute for Single Crystals, Kharkov (1984) (in Russian).
77. N. I. Shevtsov and I. I. Mirenskaya, in *Crystal Growth and Crystal Properties*, p. 100. Institute for Single Crystals, Kharkov (1984) (in Russian).

78. A. N. Smagunova, O. F. Rozova and I. M. Prekina, *Zh. Anal. Khim.* **49**, 711 (1994).
79. N. I. Shevtsov, A. B. Blank, I. I. Mirenskaya and Y. A. Obukhovskiy, *Zh. Anal. Khim.* **40**, 1807 (1985).
80. K. Iwasaki and K. Hiyoshi, *Bunseki Kagaku* **37**, T152 (1988).
81. V. V. Krasavin, L. Y. Pavlov, Y. V. Gorshkov and N. F. Bogdanovskaya, *Zavod. Lab.* **57**, No. 8, 36 (1991).
82. I. I. Kuselman, L. I. Michetina and F. A. Khubedzhev, *Zh. Anal. Khim.* **45**, 1533 (1990).
83. I. A. Grikit and E. G. Galushko, *USSR Pat.* 3 282 006 (1988).
84. Z. A. Mohamadi, *Bull. Geol. Surv. Can.*, No. 451, 1 (1993).
85. V. Kocman, *Adv. X-Ray Anal.* **30**, 243 (1987).
86. F. Claisse in *43rd Annual Denver Conference on Applied X-Ray Analysis, Abstracts*, p. 96. Steamboat Springs, CO (1994).
87. R. Jenkins and J. L. De Vries, *Practical X-Ray Spectrometry*, 2nd ed., p. 1555. Macmillan, London (1983).
88. A. S. Schlorholtz and T. Demirel, *Adv. X-Ray Anal.* **30**, 251 (1987).
89. G. Li, *Bull. Geol. Surv. Can.*, No. 451, 85 (1993).
90. A. Yoshioka, T. Sekine, H. Yoshida and K. Nomura, *Bunseki Kagaku* **37**, 595 (1988).
91. R. G. Johnson, *Adv. X-Ray Anal.* **30**, 105 (1987).
92. M. S. Fogelson, N. A. Korovkina, A. T. Savitchev and I. A. Roschina, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 354. Moscow (1990).
93. N. A. Korovkina, I. A. Roschina and E. A. Kulikovskaya, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 398. Moscow (1990); N. Korovkina, A. Maiorov, I. Roschina, A. Gouzhova, Y. Scherbovsky, L. Zholudeva and N. Kononkova, in *10th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 12. Warsaw (1988).
94. I. G. Cobo, M. T. Dorado and A. G. Coedo, *J. Trace Microprobe Tech.* **13**, 431 (1995).
95. J. Jurczyk, G. Sankiewicz, V. Helan and B. Svardalova, in *12th International Congress on X-Ray and Optical Microanalysis, Abstracts*, p. 147. Kracow (1989).
96. Z. Mao, *Fanxi Huaxue* **16**, 909 (1988).
97. B. S. W. King and S. Vivit, *X-Ray Spectrom.* **17**, 85 (1988).
98. V. A. Shvetsov and V. P. Chicheva, *USSR Pat.* 4 801 071/26 (1992).
99. M. H. Jones and B. W. Wilson, *Analyst (London)* **116**, 449 (1991).
100. H. Yuan, Y. Liu and Y. Qin, *Fanxi Huaxue* **18**, 451 (1990).
101. F. B. Reig, T. D. Carbo, V. P. Martinez and J. V. Adelantado, *Spectrochim. Acta, Part B* **43**, 811 (1988).
102. R. A. Couture, M. S. Smith and R. F. Dymek, *Chem. Geol.* **110**, 315 (1993).
103. V. Maximov and G. Savchenko, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 405. Moscow (1990).
104. A. L. Finkelshtein, *Zh. Anal. Khim.* **47**, 1709 (1992).
105. T. Fink, C. Chang and A. Janssen, *GIT* **37**, 492 (1993).
106. N. N. Naumenko, E. G. Tarasova, R. A. Filippova and N. S. Baimurzina, *Zavod. Lab.* **58**, No. 2, 53 (1992).
107. M. Lutz, W. Bywaters and P. Gokhale, in *Pittsburgh Conference, PITTCON'92, Abstracts*, p. 142. New Orleans (1992).
108. I. V. Bogdanova, V. N. Maximov and V. R. Alperovich, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 387. Moscow (1990).
109. I. P. Petrov, M. G. Dzhioeva, A. I. Khazanova and E. L. Lutsenko, *USSR Pat.* 4 134 140/25-25 (1988).
110. T. P. Blaschuk, E. V. Savina, T. P. Mamulova and V. G. Kostin, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 386. Moscow (1990).
111. V. A. Kjutvitsky, Y. M. Glubokov, V. V. Borisova, E. V. Mironova and W. Manasreh, in *10th Conference on the Chemistry of High-Purity Substances, Abstracts*, p. 163. Nizhny Novgorod (1995); V. A. Kjutvitsky, L. M. Chernyshova, M. B. Bobkova, V. V. Borisova, E. V. Mironova and W. Manasreh, in *10th Conference on the Chemistry of High-Purity Substances, Abstracts*, p. 164. Nizhny Novgorod (1995).
112. A. I. Belogorokhov, V. V. Borisova, V. A. Kjutvitsky and W. Manasreh, *J. Mol. Struct.* **349**, 455 (1995).
113. V. A. Kjutvitsky, V. A. Manasreh, L. M. Chernysheva and M. V. Bobkova, *Russ. Pat.* 2 054 661 (1966).
114. L. P. Eksperiandova, S. F. Kvjatkovsky, K. F. Kravtsova, N. I. Shevtsov and A. B. Blank, *Zh. Anal. Khim.* **47**, 937 (1992).
115. Y. K. Kvartskheli and I. V. Kornienko, *Zavod. Lab.* **58**, No. 12, 17 (1992).
116. V. A. Simakov, N. S. Vakhonin and V. E. Isajev, *Zavod. Lab.* **62**, No. 8, 19 (1996).
117. V. A. Shestakov, V. V. Golubchikov, I. A. Gerzkin and E. G. Namvrina, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 415. Moscow (1990).
118. P. K. Govil, *Bull. Geol. Surv. Can.*, No. 451, 16 (1993).
119. B. T. Eddy and A. M. E. Balaes, *X-Ray Spectrom.* **17**, 17 (1988).
120. Y. Matsumoto, M. Yamaji and N. Fujino, *Bunseki Kagaku* **37**, T50 (1988).
121. K. Mizukami, S. Kasai, N. Kasai and K. Amakawa, *Bunseki Kagaku* **37**, 607 (1988).
122. Y. Kobayashi and S. Nakamura, *Bunseki Kagaku* **38**, T85 (1989).
123. G. Panayotov, in *11th Conference Analytical Atomic Spectroscopy, Abstracts*, p. 408. Moscow (1990).
124. R. T. Rutherford, *X-Ray Spectrom.* **24**, 109 (1995).
125. N. I. Shevtsov, A. B. Blank, I. I. Mirenskaya and Z. M. Nartova, *USSR Pat.* 4 672 592/24-25 (1990); *Russ. Pat.* 1 824 024 (1993).
126. V. I. Karmanov, N. S. Slobodyanik, P. G. Nagorny and O. P. Ryabushko, *Zh. Anal. Khim.* **46**, 121 (1991).
127. H. Ehrhardt and P. Dittrich, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 351. Moscow (1990).
128. A. B. Blank, N. I. Shevtsov, I. I. Mirenskaya and Z. M. Nartova, *Zh. Anal. Khim.* **45**, 1724 (1990).
129. Z. M. Spolnik, P. V. Mateichenko, N. I. Shevtsov and A. B. Blank, *Zh. Anal. Khim.* **48**, 1599 (1993).
130. N. I. Shevtsov, Z. M. Nartova, L. A. Kvichko and A. B. Blank, *Zh. Anal. Khim.* **46**, 591 (1991).
131. G. Kaiser, A. Meyer, M. Friss, R. Riedel, M. Harris, E. Jacob and G. Tölg, *Fresenius' J. Anal. Chem.* **352**, 318 (1995).
132. T. G. Rao and P. K. Govil, *Analyst (London)* **120**, 1279 (1995).
133. I. V. Kornienko, *USSR Pat.* 4 051 275/40-25 (1990).
134. K. Sugimoto, T. Akiyoshi and T. Kondou, *Bunseki Kagaku* **37**, 589 (1988).
135. A. M. Samarina and A. P. Nikolsky, *Zavod. Lab.* **55**, No. 12, 23 (1989).
136. *Zavod. Lab.* **61**, No. 5, 58 (1995).
137. A. B. Blank, V. T. Vlasov, Z. M. Nartova and N. I. Shevtsov, *Zh. Anal. Khim.* **42**, 358 (1987).
138. I. I. Mirenskaya, N. I. Shevtsov, A. B. Blank, L. L. Nagornaya, Z. M. Spolnik and O. V. Gaiduk, *Zh. Anal. Khim.* **49**, 522 (1994).
139. P. Hoffmann, S. Buchta-Hohm and B. Sasse, *Fresenius' J. Anal. Chem.* **331**, 423 (1988).
140. D. Dimitrov, *Khim. Ind.* **60**, 290 (1988).
141. M. Solazzi, *US Pat.* 4 665 759 (1987).
142. B. Koltunov, J. Lantzsch, G. Kießig, C. Weissbach and B. Schafer, *E. Ger. Pat.* DD 295 919 (1991).
143. Yu Liang and Lichua Jianyan, *Huaxue Fence* **26**, 157 (1990).
144. N. Cornejo, A. Afailal, F. Garcia and M. Palacios, *Fresenius' J. Anal. Chem.* **350**, 122 (1994).
145. P. S. Dhami, V. Gopalakrishnan, A. Ramanujam, R. K. Dhumwad and B. S. Negi, in *BARC [Rept]*, No. E006, p. 1 (1993); from *Ref. Zh., Khimiya Abstr.* 5G195 (1995).
146. E. G. Khomutova, L. M. Chernyshova, L. I. Yuranova and A. G. Sychov, *Zavod. Lab.* **55**, No. 12, 26 (1989).
147. I. Hanif, J. Hanif, R. Quadeer and M. Z. Iqbal, *J. Radioanal. Nucl. Chem. Art.* **191**, 305 (1995).
148. V. P. Seminozhenko, V. F. Khirnyi, N. I. Shevtsov, P. V. Mateichenko, A. A. Kozlovsky, T. S. Teplitskaya, Y. P. Shokurov and S. Y. Sumarokov, *Funct. Mater.* **1**, 19 (1994).
149. A. B. Blank, O. V. Gaiduk, T. V. Druzenko, R. P. Pantaler, V. G. Potapova, S. Y. Sumarokov, L. I. Filippovich and N. I. Shevtsov, *Zh. Anal. Khim.* **51**, 547 (1996).
150. S. D. Pan'kov, A. P. Markov, G. G. Markova, N. Z. Nasyrov and A. N. Smagunova, *USSR Pat.* 1594371 (1990).
151. O. I. Lyamina, T. A. Kuprianova and F. A. Gimelfarb, *Zh. Anal. Khim.* **50**, 271 (1995).
152. L. P. Eksperiandova, Z. M. Spolnik and A. B. Blank, *Adv. X-Ray Anal.* **38**, 735 (1995).
153. L. P. Eksperiandova, A. B. Blank and Y. N. Makarovskaya, in *45th Annual Denver X-Ray Conference, Abstracts*, p. 35.

- Denver, CO (1996).
154. L. P. Eksperiandova, A. B. Blank, I. I. Potapova and Y. N. Makarovskaya in *45th Annual Denver X-Ray Conference, Abstracts*, p. 36. Denver, CO (1996).
  155. M. Mantler and T. Taut, *X-Ray Spectrom.* **18**, 105 (1989).
  156. K. G. Shcherbakov and F. A. Gimelfarb, *Zh. Anal. Khim.* **48**, N 11, 137 (1993).
  157. V. F. Volkov, E. B. Semenova, S. A. Gerasimov and V. N. Sinitsin, *Zavod. Lab.* **54**, No. 12, 46 (1988).
  158. A. G. Pyatakov, V. P. Gordienko and V. M. Azarov, *Zavod. Lab.* **55**, No. 2, 47 (1989).
  159. J. Renault and C. McKee, *Analyst (London)* **120**, 1261 (1995).
  160. M. Zhang, Y. Fan, W. Strang and X. Huang, *Fanxi Huaxue* **16**, 660 (1988).
  161. C. Boni, A. Caride, E. Cereda, M. G. Braga Marcazzan and R. Redealli, *Nucl. Instrum. Methods Phys. Res. B* **49**, 106 (1990).
  162. P. Wobrauschek, C. Strel, P. Kregsamer, W. Ladisich and R. Rieder, *J. Trace Microprobe Tech.* **14**, 103 (1996).
  163. J. A. van Khan and R. D. Vis, *X-Ray Spectrom.* **24**, 58 (1995).
  164. H. Hashimoto, Y. Iida, H. Saisho and H. Nishioji, *Anal. Sci.* **7**, Part 1, Suppl., 577 (1991).
  165. C. T. Yap and K. V. R. Gunawardena, *Appl. Spectrosc.* **43**, 702 (1989).
  166. R. Klockenkamper and A. von Bohlen, *J. Anal. At. Spectrom.* **7**, 273 (1992).
  167. A. Prange, *Spectrochim. Acta, Part B* **44**, 437 (1989).
  168. A. Prange and H. Schwenke, *Adv. X-Ray Anal.* **32**, 211 (1988).
  169. J. Injuk and R. Van Grieken, *Spectrochim. Acta, Part B* **50**, 1787 (1995).
  170. C. Strel, P. Wobrauschek, W. Ladisich, R. Rieder and H. Aiginger, *X-Ray Spectrom.* **24**, 137 (1995).
  171. B. Schneider, *Spectrochim. Acta, Part B* **44**, 519 (1989).
  172. M. Necemer, P. Kump and B. Stropnik, *Acta Chim. Slov.* **43**, No. 1, 61 (1996).
  173. R. Klockenkamper, A. von Bohlen and B. Wiecken, *Spectrochim. Acta, Part B* **44**, 511 (1989).
  174. L. Fabry, S. Pahlke and L. Kotz, *Fresenius' J. Anal. Chem.* **354**, 266 (1996).
  175. Q. Fan, J. Lin and C. Wei, *Fresenius' J. Anal. Chem.* **354**, 193 (1996).
  176. P. K. Patra, L. Madan, H. N. Bajpai and I. Daisy, *BARC [Rept]* No. P006, p. 85 (1993); from *Ref. Zh., Khimiya Abstr.* 7G140 (1995).
  177. I. Calliari, G. Caniglia, S. Nardi, A. M. Tollardo and R. Callegaro, *X-Ray Spectrom.* **24**, 143 (1995).
  178. H. N. Thi, H. N. Viet and J. Boman, *J. Trace Microprobe Tech.* **14**, 153 (1996).
  179. E. A. Marier, M. L. Sargentini-Marier, F. Rasteyar, C. Christophe, C. Ruch, R. Heimbürger and M. J. F. Leroy, *Fresenius' Z. Anal. Chem.* **331**, 58 (1988).
  180. D. C. Johnson in *Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, Abstracts*, p. 063P, Chicago (1994).
  181. A. B. Blank, L. E. Belenko and N. I. Shevtsov, *Zh. Anal. Khim.* **41**, 286 (1986).
  182. M. K. Beklemishev, L. I. Gorodilova, N. I. Shevtsov, L. M. Kardivarenko and N. M. Kuz'min, *Zh. Anal. Khim.* **44**, 1058 (1989).
  183. A. B. Blank, L. P. Eksperiandova, V. V. Aliseichik and N. I. Shevtsov, *Zh. Anal. Khim.* **45**, 1843 (1990).
  184. D. Gallop and J. Medved, *Nucl. Instrum. Methods Phys. Res. B* **49**, 313 (1990).
  185. T. Stafilov and T. Todorovski, *Zb. Rad. Techn. Fak. Inst. Bakar. Bor.* **24**, 199 (1988); from *Ref. Zh., Khimiya, Abstr.* 16G184 (1989).
  186. A. P. Markov, *USSR Pat.* 4 161 686/23-25 (1988).
  187. S. Kurozumi, S. T. Abe, H. Maruyama and Y. N. Yachiyo, *US Pat.* 4 788 700 (1988).
  188. S. Zhong, Z. Yuefen and Z. Jipei, *Fanxi Huaxue* **18**, 84 (1990).
  189. M. A. Scapin and S. V. L. Ribeiro, *Instituto de Pesquisa de Energia Nuclear. Publicações (Brazil)*, No. 270, 1 (1989); from *Ref. Zh., Khimiya, Abstr.* 19G221 (1990).
  190. R. D. Govier, *Rep. Invest. Bur. Mines US Dep. Inter.*, No. 9254, 1 (1989).
  191. L. L. Bepalova, L. A. Mandryna, A. A. Kozhanova and M. V. Koloskova, *Zavod. Lab.* **57**, No. 7, 68 (1991).
  192. N. A. Gal'tsev, B. S. Iokhin, C. L. Levulin and V. I. Khorev, *At. Energ.* **69**, 117 (1990).
  193. J. C. Jaffredo, J. L. Colin, H. Lazar and G. Mouvier, *Analisis* **17**, 443 (1989).
  194. T. A. LaFisca, S. I. Nagourney and C. Pietarinen, *Talanta* **38**, 995 (1991).
  195. A. F. Ermakov, V. N. Zakharov and I. I. Kondrat'ev, in *11th Conference Analytical Atomic Spectroscopy, Abstracts*, p. 389, Moscow (1990).
  196. J. C. Gallao and R. Quillermo, *Analisis* **17**, 576 (1989).
  197. C. F. Wang, E. E. Chang, P. C. Chiang and N. K. Aras, *Analyst (London)* **120**, 2521 (1995).
  198. Y. Inokuma and J. Endo, *Bunseki Kagaku* **37**, 503 (1988).
  199. V. Bhagavathy, P. S. T. Sai, T. P. Rao and A. D. Damadaran, *Anal. Lett.* **22**, 197 (1989).
  200. Rajeev and J. Muralidhar, *X-Ray Spectrom.* **18**, 211 (1989).
  201. H. Iwaya, Y. Maeda and T. Arumi, *Nippon Kaisui Yakkashii* **43**, 212 (1989).
  202. S. Peraniemi, J. Vepsäläinen, H. Mustalahti and M. Anlgren, *Fresenius' J. Anal. Chem.* **344**, 118 (1992).
  203. Y. Iwata, Y. Ishibashi, N. Gunji and H. Yoshikawa, *Bunseki Kagaku* **40**, 361 (1991).
  204. B. T. Eddy and A. M. E. Balaes, *X-Ray Spectrom.* **17**, 195 (1988).
  205. N. Kurata, Y. Harada and G. Furuno, *Bunseki Kagaku* **38**, 193 (1989).
  206. M. Nagj, J. Injuk and V. Valkovic, *J. Radional. Nucl. Chem. Lett.* **127**, 243 (1988).
  207. T. Tisue, C. Seils and R. T. Keel, *Anal. Chem.* **57**, 82 (1985).
  208. N. A. Korovkina, I. A. Rostchina, A. P. Majorov, V. F. Rone, D. K. Vircava and M. V. Vircavs, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 399, Moscow (1990).
  209. V. N. Sinitsin, E. V. Semionova and O. M. Aleksanjan, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 416, Moscow (1990).
  210. G. Engel, R. Ostner and H. Bebnier, *Chem.-Ztg.* **113**, 382 (1989).
  211. Y. Taira, Y. Maeda and T. Azumi, *Nippon Kaisui Gakkaishi* **42**, 109 (1988).
  212. I. Y. Andreeva, N. G. Polivanova and D. N. Bogomolova, *Zh. Anal. Khim.* **47**, 383 (1992).
  213. I. Y. Andreeva and S. V. Drogobuzhskaya, *Zh. Anal. Khim.* **45**, 904 (1990).
  214. M. V. Melkonyan, O. O. Dadyka and Z. A. Tamerdashev, in *All-Russian Conference Environmental Analysis, Abstracts*, p. 76, Krasnodar (1994).
  215. I. F. Seregina, G. I. Tsisin, A. M. Shilnikov, A. A. Formanovsky and Yu. A. Zolotov, *Zh. Anal. Khim.* **48**, 166 (1993).
  216. A. V. Terletskaya, T. A. Bogoslavskaya, A. E. Borzakovskiy, O. L. Stikhar' and I. A. Ageeva, *Khim. Tekhnol. Vody* **15**, 435 (1993).
  217. A. Khuder, L. P. Maslov and V. A. Kjutvitsky, *Zh. Anal. Khim.* **51**, 121 (1996); *Vysokochist. Veshchestva*, No. 1, 121 (1996).
  218. N. V. Kulagina, T. I. Tikhomirova, H. M. Sorokina, V. I. Fadeeva, G. I. Tsisin and Y. A. Zolotov, *Vestn. Mosk. Univ., Khimia* **35**, 167 (1994).
  219. E. Zhao and L. Qiu, *Lihua Jianyan Huaxue Fence* **30**, 106 (1994).
  220. J. N. Driscoll, C. Wood and E. Ekmejian, in *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Abstracts*, p. 1183, Atlanta, GA (1993); J. N. Driscoll, C. Wood, E. Ekmejian and T. Spittler, in *Pittsburgh Conference, PITTCON'92, Abstracts*, p. 288, New Orleans (1992).
  221. A. N. Smagunova, L. V. Morozov and B. A. Trofimov, *Zh. Anal. Khim.* **43**, 84 (1988).
  222. Y. Guo, Y. Zhang, M. Zhou and Q. Wei, *Jilin Daxue Ziran Kexue Xuebao*, No. 1, 98 (1988).
  223. K. Beeg, R. Sub, H. Bruchertseifer, F. Loth, S. Fisher and S. Rostler, *ZFI-Mitt.*, No. 165, 60 (1991).
  224. K. Moriyasu, H. Mizuta and Y. Nishikawa, *Bunseki Kagaku* **40**, 175 (1991).
  225. V. Bhagavathy, M. L. P. Reddy, P. S. T. Sai, T. P. Rao and A. D. Pamodaran, in *Proceedings of Symposium, TMS Annual*

- Meeting, p. 717. Warrendale, PA (1988).
226. E. G. Khomutova, L. P. Zytchenko, A. P. Rysev and A. A. Dilektorsky, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 393. Moscow (1990).
227. E. B. Semenova, K. N. Bogdasarov and G. E. Blokhina, *Zavod. Lab.* **54**, No. 4, 33 (1988).
228. V. P. Khvostova, V. A. Trunova, V. B. Baryshev and K. V. Zolotarev, *Nucl. Instrum. Methods Phys. Res. A* **308**, 315 (1991).
229. S. Peraniemi, J. Parkkinen, K. Smolander, H. Mustalahti and M. Anlgren, *Fresenius' J. Anal. Chem.* **343**, 292 (1992).
230. P. S. Dhami, B. L. Jangida and M. Sundaresan, *J. Radioanal. Nucl. Chem. Art.* **141**, 437 (1990).
231. M. M. Frolova, I. P. Golentovskaya, A. N. Smagunova, V. F. Zagumenova, L. B. Morozova and B. A. Trofimov, *Zavod. Lab.* **57**, No. 8, 33 (1991).
232. V. Bhagavathy, M. L. P. Reddy, T. Prasada Rao and A. D. Damodaran, *J. Radioanal. Nucl. Chem. Art.* **149**, 35 (1991).
233. N. I. Shcherbinina, G. R. Ishmiyarova, I. E. Nikitina, G. V. Myasoedova, L. A. Polosukhina, I. I. Uralov, A. D. Simonova and E. Y. Danilova, *Zh. Anal. Khim.* **45**, 766 (1990).
234. A. G. Revenko, S. A. Volodin and A. I. Uvarov, *Zavod. Lab.* **57**, No. 4, 29 (1991).
235. V. I. Uvarov, S. A. Volodin and A. G. Revenko, *Zavod. Lab.* **54**, No. 9, 45 (1988).
236. M. A. Tarig and I. L. Preiss, *J. Radioanal. Nucl. Chem. Art.* **163**, 355 (1992).
237. N. Sen, N. K. Roy and A. K. Das, *Indian J. Technol.* **27**, 366 (1989).
238. N. Sen, N. K. Roy and A. K. Das, *Talanta* **36**, 697 (1989).
239. S. A. Logunova, F. I. Lobanov, I. N. Sarzhenko, L. A. Karpova and E. S. Akberdina, *Zh. Anal. Khim.* **50**, 994 (1995).
240. A. I. Zebrev, Y. E. Kurilovich, F. I. Lobanov and N. N. Andreeva, *Zh. Anal. Khim.* **47**, 629 (1992).
241. E. Zlobina, A. Zebrev, N. Ivanova and L. Filippova, in *35th IUPAC Congress, Abstracts, Part 2*, p. 1144. Istanbul (1995).
242. F. I. Lobanov, V. A. Zakharov, S. S. Dosmagametov and B. N. Myzagalieva, *Zavod. Lab.* **58**, No. 6, 1 (1992).
243. A. I. Zebrev, N. V. Ivanova and L. M. Filippova, in *International Solvent Extraction Conference, Abstracts*, p. 200, Kyoto (1990).
244. A. I. Zebrev, N. N. Andreeva, F. I. Lobanov, O. A. Manuilova and Y. A. Il'yukevich, *Zavod. Lab.* **57**, No. 6, 19 (1991).
245. F. I. Lobanov, N. N. Andreeva, N. V. Ivanova, A. I. Zebrev, L. M. Filippova and Y. A. Il'yukevich, *Zavod. Lab.* **57**, No. 6, 18 (1991).
246. F. I. Lobanov, A. K. Nurtaeva, A. V. Stefanov, L. D. Londer' and N. V. Makarov, *USSR Pat.* 3 947 983/31-26 (1988).
247. N. D. Londer', A. V. Stefanov and F. I. Lobanov, in *Ecological Symposium, 'Water Analysis', Abstracts*, p. 55, Voronezh (1990).
248. F. I. Lobanov, S. S. Dosmagambetova, V. A. Leonov, A. K. Nurtaeva and V. V. Yakshin, in *International Solvent Extraction Conference*, Vol. 4, p. 82. Moscow (1988).
249. F. I. Lobanov, A. I. Zebrev, N. N. Andreeva, S. A. Logunova, T. A. Pasynkova, O. A. Manuilova and Y. E. Kirilovich, in *11th Conference on Analytical Atomic Spectroscopy, Abstracts*, p. 402. Moscow (1990).
250. S. A. Logunova, N. M. Dolgova, N. N. Andreeva and E. S. Akberdina, in *35th IUPAC Congress, Abstracts II, Sect. 4-6*, p. 1087. Istanbul (1995).
251. S. Y. Sumarokov, N. I. Shevtsov and A. B. Blank, *Zh. Anal. Khim.* **47**, 1727 (1992).
252. V. A. Surnin, O. V. Astaf'ev and N. N. Badovskaya, in *International Conference, Technological Systems for Ecological Safety, Abstracts*, p. 73, Leningrad (1991).
253. L. P. Eksperiandova, A. B. Blank, Y. N. Chumak, in *10th Conference on the Chemistry of High-Purity Substances, Abstracts*, p. 168. Nizhny Novgorod (1995).
254. A. B. Blank, *Pure Substances Analysis with Crystallization Preconcentration*. Khimiya, Moscow (1986) (in Russian).