

# Trends in Sorption Preconcentration Combined with Noble Metal Determination

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Nowadays much attention is being paid to the determination of trace amounts of noble metals in geological, industrial, biological and environmental samples. The most promising techniques, such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and electrothermal atomic absorption spectrometry (ETAAS) are characterized by high sensitivity. However, the accurate determination of trace noble metals has been limited by numerous interferences generated from the presence of matrix elements. To decrease, or eliminate, these interferences, the sorption preconcentration of noble metals is often used prior to their instrumental detection. A great number of hyphenated methods of noble metal determination using sorption preconcentration have been developed. This review describes the basic types of available sorbents, preconcentration procedures and preparations of the sorbent to the subsequent determination of noble metals. The specific features of instrumental techniques and examples of ETAAS, FAAS, ICP-AES, ICP-MS determinations after the sorption preconcentration of noble metals are considered. The references cited here were selected mostly from the period 1996 – 2006.

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## 1 Introduction

The demand for noble metals in different areas, such as industry, technology and medicine is constantly growing. Namely this tendency, along with the high cost of platinum-containing materials, makes the requirements concerning the efficiency of noble metal determination tougher for a wide variety of materials.<sup>1-3</sup> Accurate determinations of noble metal traces have become increasingly necessary to solve new problems connected with the deposit evaluation, secondary material processing, environmental pollution, analysis of biological and other objects. At the same time, it is a very difficult analytical task due to the complicated chemistry of noble metals and matrices containing its traces.<sup>1,4-7</sup>

A number of recent reviews have shown that the most promising techniques for the determination of platinum metals and gold are highly efficient multi-element methods based upon inductively coupled plasma (ICP-MS and ICP-AES). ETAAS is also widely used, usually in a single-element mode, and ensures excellent detection limits. X-Ray fluorescence (XRF),

neutron activation analysis (NAA) and other methods are used comparatively rarely.<sup>8-12</sup>

In spite of the high sensitivity of the modern instrumentation, the direct analysis of real samples is considerably restricted owing to interferences caused by matrix elements. A radical way to eliminate matrix effects is a preliminary separation of macrocomponents by a relative, or absolute, preconcentration of noble metals. Preconcentration procedures allow one to decrease the detection limits while unifying the analytical schemes for materials of different nature, and simplifying the preparation of calibration samples, as well as improving the reliability of analysis.<sup>13-16</sup>

There are different techniques of noble metal preconcentration: fire assay using various collectors, precipitation and coprecipitation, extraction, sorption, *etc.*<sup>1,3</sup> Sorption preconcentration is one of the most effective methods for these metals.<sup>17,18</sup> In recent years, complexing (chelating) sorbents and ion exchangers are widely used for noble metal preconcentration.<sup>19,20</sup> In cases where extremely low noble metal contents and their heterogeneous distribution exist, samples of large mass are required. During the analysis of large samples, combined procedures have been applied: for example, a fire assay using nickel sulfide, followed by dissolution of the button with acids and the sorption preconcentration of noble metals.<sup>21,22</sup>

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Sorption preconcentration is extensively applied in a combination with various instrumental techniques, such as ETAAS, ICP-AES, and ICP-MS. Obviously, in these cases, the efficiency of the noble metal determination depends on the characteristics of the sorbent and the preconcentration conditions. Taking into account the importance of the sorption procedures in the given review, we have considered the various types of sorbents, the features of the static and dynamic modes of preconcentration, as well as the methods of sample digestion and the techniques of sorbent/solution preparation to the subsequent determination. Some features of the instrumental methods for the determination of noble metals have also been surveyed.

## 2 Sorbents and Preconcentration Procedures

Sorption preconcentration is usually carried out after the dissolution of solid samples. The choice of an appropriate digestion method depends on the kind of sample matrix, the nature of the element and its speciation, and other factors.<sup>3</sup> Thus, alkali fusion provides soluble salts of most of geological materials.<sup>23-25</sup> Dry ashing followed by dissolution of the residue with acids is often used for the digestion of biological, environmental and clinical samples.<sup>26-28</sup> Acid dissolution is extensively used for the digestion of different matrices, and can be carried out in open or closed systems, such as high-pressure ashers (HPA)<sup>29-31</sup> or high-pressure vessels heated by microwaves.<sup>32-35</sup> Microwave techniques are especially effective for the dissolution of samples with a high content of organic matter, for example, carbonaceous shales, biological materials, pharmaceuticals and others.<sup>9,36,37</sup> The quantitative conversion of noble metals into suitable complexes, along with complete dissolution, is another critical step in almost all analytical procedures. The sorption preconcentration of noble metals is usually carried out from hydrochloric acid solutions (frequently 0.1–3 M), in which these metals exist as sorption-active chloride or aqua-chloride anionic complexes.<sup>1</sup> Chlorination and boiling with aqua regia or hydrochloric acid are often necessary for the conversion of noble metals into chloride complexes.<sup>2,3</sup> However, the preconcentration of noble metals from other solutions, for example nitrate ones, is also of interest since nitric acid is often applied to the dissolution of analyzed samples.

Different types of sorbents have been synthesized for the preconcentration of noble metals: complexing sorbents, ion exchangers, coals, biosorbents, *etc.* The widest application has found sorbents with ion-exchanging and complex-forming functional groups. Anion exchangers based on polymeric or mineral matrices usually contain amine groups of various basicity.<sup>38-42</sup> Strongly basic anion exchangers with quaternary amine groups, such as Dowex 1-X8, AG 1-X8, are the most used for the preconcentration of noble metals.<sup>29,35,43-47</sup> Weakly and intermediate basic anion exchangers (Amberlite IRA 93, Duolite S 37, HHY-10A, *etc.*) have also been applied.<sup>48-53</sup> The sorption recovery of noble metals from hydrochloric solutions by ion-exchanging sorbents is mainly a result by ion exchange. However, the complex-formation of noble metals with nitrogen atoms of anion exchangers under sorption is also possible.<sup>38</sup>

Selectivity is one of the most important characteristic of sorbents.<sup>20</sup> From this point of view, the preferable ones are complexing nitrogen-containing sorbents, which ensure high selectivity towards gold and platinum metals in acid solutions.<sup>1,54</sup> Complexing sorbents destined for noble metal preconcentration are synthesized in different ways: the chemical modification of polymeric and mineral matrices (grafting of functional groups) or the non-covalent immobilization of

reagents (ligands) on various supports.<sup>19,55-58</sup> Recently, the sorbents prepared by the non-covalent immobilization of organic complex-forming and ion-exchanging reagents on the surface of polymeric supports and silica gels have gained considerable attention.<sup>16,17,59-62</sup> Many complexing sorbents with different functional groups have been proposed for the preconcentration of noble metals, mainly with nitrogen- and sulfur-containing groups, including imidazole, pyrazole, pyridine, thiazole, *etc.* Sorbents with amidoxime, thioamide, dithione, mercapto- and other groups have also been used.<sup>63-102</sup>

The sorption by complexing sorbents is accompanied by the formation of complexes of noble metals with functional groups of sorbents, which allows selectively to extract noble metals from complex solutions. Ion exchange and the reduction of noble metals to the lowest oxidation level are also possible during sorption. In fact, the mechanism of the interaction of noble metals with complexing sorbents is complicated, and depends on both the type of complex-forming groups and the sorption conditions. In many cases it has not been investigated sufficiently.

The sorption capacity and kinetic characteristics as well as the mechanical and chemical stability of sorbents in solutions are generally caused by properties of the matrix, and also by the form of sorbents (powders, granules, fibers, *etc.*). The synthesis method and the kind of a matrix have a profound effect on the sorptive properties of sorbents.

The sorbents can be used in a form of finely dispersed powders, granules, fibers and various composite materials.<sup>14</sup> Fibrous sorbents are possessed by sufficient selectivity together with good kinetic properties, and a convenient form for sorption applications. A wide variety of fibrous sorbents with different complexing groups are synthesized for the preconcentration of noble metals, mainly on a base of polymeric matrices. A new type of complexing sorbents with a fibrous structure is “filled” fibrous materials, which are characterized by good kinetic and filtering properties and high selectivity to noble metals. These materials consist of two polymers: highly porous polyacrylonitrile fiber and filler—finely dispersed powder of complexing sorbents or ion exchangers. The filler is strongly kept in a thin porous polyacrylonitrile fiber, which ensures the efficiency of sorption recovery.<sup>63,103</sup>

Along with complex-forming and anion-exchanging sorbents, a number of different ones, such as activated coals,<sup>104-106</sup> natural and synthetic zeolites,<sup>107</sup> modified chitozanes,<sup>108-111</sup> biosorbents,<sup>112-114</sup> *etc.* have been investigated for the preconcentration of noble metals.

The choice of a sorbent and sorption mode for the preconcentration of noble metals depends on the nature of the examined sample, its weight and the volume of the solution obtained after decomposition of the sample and its salinity. It is very important to take into account the characteristics of the sorbent and its cost, as well as the requirements of the following determination (sensitivity, selectivity, possibility of the direct analysis of concentrate, *etc.*). For an effective sorption of noble metals, keeping definite conditions is necessary: the pH or acid concentration, the temperature and the contact time of phases at a bath experiment or the flow rate of the solution through a sorbent layer during dynamic preconcentration.<sup>1</sup>

The static mode is used mainly for routine analysis. The necessary conditions to be maintained under the static mode are the ratio of the solution volume to the sorbent mass, the contact time of the phases and the temperature, which depend on the kinetic properties of the sorbent and the activity of the ionic forms of noble metals. It is known that noble metals exist in solutions as different complexing forms, which are distinguished

by various kinetic activities according to the oxidation state of the central atom, the kind and concentration of the acid and other ligands, duration of storage of the solution, *etc.*<sup>115-118</sup> Long heating or other methods of activation are required for the preconcentration of kinetic inert complexes, especially complexes of rhodium and iridium. Different approaches are used to intensify their preconcentration. For example, the recovery of hardly sorbed rhodium essentially increases when tin chloride is added in a solution during sorption and extraction.<sup>119,120</sup> Microwaves, ultraviolet radiation or ultrasound can be used to facilitate noble metal sorption and to decrease the contact time under the preconcentration.<sup>104,121</sup> Thus, microwave-assisted sorption ensures a complete recovery of gold, palladium, platinum, rhodium, iridium and ruthenium by complexing sorbent POLYORGS 4 from hydrochloric and nitric acid solutions (1 M HCl or 1 M HNO<sub>3</sub>) within 15 min.<sup>122,123</sup> Under the usual conditions, it is impossible to achieve a quantitative recovery of platinum metals (especially from nitric acid solutions), and it takes a long contact time under thermal heating.

The dynamic mode, in part, on-line system is currently applied in combined methods. For the preconcentration of noble metals in a dynamic regime, sorbents have to be distinguished by good kinetic properties. Sorbents with non-covalently bound reagents are often used for on-line preconcentration due to fast sorption and the possibility of fast elution. For the dynamic preconcentration “filled” fibrous sorbents POLYORGS are very suitable. These non-woven fibrous materials in a form of disks (filters) are especially convenient for the dynamic preconcentration and subsequent determination of noble metals on a sorbent phase directly.<sup>124</sup> Mathematical modelling has been applied to optimize the dynamic parameters of the noble metal preconcentration by “filled” fibrous POLYORGS sorbents.<sup>125</sup> Thus, the conditions of dynamic preconcentration (sample volume, sorbent mass, height of layer, flow rate of the solution) were determined for platinum and palladium sorption by POLYORGS 17-n.<sup>126</sup>

The preparation of a sorbent after preconcentration is very important for noble metal determination by instrumental methods. The sorbent can be analyzed in a solid state, or as a solution obtained either after sorbent decomposition or after the elution of noble metals. For ETAAS, FAAS, ICP-AES and ICP-MS analyses, the dissolved substances are preferable.<sup>37</sup> In many cases the elution of noble metals by acids or thiourea is carried out.<sup>22,29,35,45,127-132</sup> However, the determination of noble metals in thiourea solutions can be hampered, and additional options, such as high dilution, are necessary.<sup>44</sup> For the desorption of noble metals after preconcentration by sorbents with non-covalently bound reagents, organic eluents (methanol, ethanol) can be used. In this case, noble metals are desorbed together with a complex-forming reagent.<sup>33,62,81</sup> When complexing sorbents are applied, the elution of noble metals is difficult or impossible. That is why the sorbents are usually decomposed by different ways. For example, the sorbents after preconcentration are decomposed by dry ashing in a muffle furnace (400–600°C), and then the residues are dissolved with acids.<sup>26,28,133-135</sup> The sorbent can be decomposed by wet ashing under boiling with a mixture of acids (HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>), and in some cases with the addition of H<sub>2</sub>O<sub>2</sub>.<sup>136</sup> The microwave decomposition of sorbents with acids in open and closed vessels has also been proposed.<sup>79,137,138</sup> It is a very promising tool of sorbent preparation for the subsequent determination of elements, because of its simplicity and rapidity. The use of closed vessels allows one to decrease any possible contamination of the concentrate.

The features of instrumental techniques and their applications for noble metal determination are considered below.

### 3 Instrumental Techniques Coupled with Sorption Preconcentration

#### 3-1 Atomic absorption spectrometry

Atomic absorption spectrometry (AAS) with flame and electrothermal atomization is one of the most widely used techniques for the determination of trace noble metals in various materials. The more efficient electrothermal atomic absorption spectrometry (ETAAS) possesses a sensitivity that is two orders higher than that of flame atomic absorption spectrometry (FAAS). The ETAAS detection limits for “easy” platinum metals are comparable with an ICP-MS determination.<sup>1,139-143</sup> In spite of a relatively short working range and an inefficient single-element mode, atomic absorption analysis is one of the most dynamic developing areas of spectrometry. It is made possible by relative simplicity, reliability and the low cost of atomic absorption spectrometers.<sup>142</sup>

Several approaches are used to correct for any non-selective background absorption: the dilution of samples, calibration on solutions with a composition equal to the sample, spike techniques, *etc.*<sup>139</sup> For an instrumental correction of the molecular background absorption, the Zeeman effect, the Smith-Hieftje technique, or a source of a continuous spectrum (for example, deuterium) are applied. A more difficult task is to eliminate any interferences caused by chemical interactions of noble metals with accompanying impurities at the different stages of the analytical cycle. For example, noble metal intermetallides possess high dissociation energies, which results in a reduced atomization efficiency. The greatest influence on noble metal determination, especially iridium and ruthenium, is exerted from the iron, nickel and copper, which are often present in real objects as basic components.<sup>37</sup>

The sorption preconcentration is often able to eliminate matrix effects. Many combined techniques based on sorption, including on-line preconcentration, are proposed for noble metal determination by FAAS or ETAAS. The combination ETAAS with sorption preconcentration was shown to be prospective for the determination of ppb – ppm levels of noble metals in geochemical objects (chromites, sulfide copper-nickel ores, industrial products), natural water samples with a high salt content, technological solutions, as well as environmental samples of different origin (soils, plants, road dust), *etc.* Sorbents of different types have been applied: ion exchangers, complex-forming sorbents, modified silica gels and others. The determinations of noble metals are usually carried out in solutions after the elution of noble metals, or after decomposition of the sorbent. The slurry sampling technique for the determination of noble metals by ETAAS in the sorbent after preconcentration (in the form of suspension in water or dimethylformamide) has also been proposed.<sup>144</sup> Examples of AAS applications for the determination of noble metals in various objects using the sorption preconcentration are given in Table 1 and in original papers.<sup>23,27,31-33,81,82,84-88,112,114,122,130,133,134,136,144-150</sup>

#### 3-2 Inductively coupled plasma atomic emission spectrometry

The multielement ICP-AES technique is characterized by good reproducibility and high efficiency.<sup>151</sup> A distinctive feature of this method is a low susceptibility to chemical interferences, caused by the high temperature of the source, *i.e.* tolerance to the matrix composition. Some restrictions of the method are connected mainly with numerous spectral overlappings.<sup>2</sup> For example, gold determination on 242.795 nm is hampered by interferences from manganese, cobalt, vanadium and iron (Mn 242.798, Co 242.829, V 242.828, Fe 242.83 nm);

Table 1 Noble metal determination by AAS coupled with sorption preconcentration

Sample	Analyte	Sorbent	Preconcentration		Sorbent preparation	Detection limit or range of metal determination	Ref.
			Solution	Mass of sorbent, mode, contact time or flow rate			
Platinum ore (CRM SARM-7), copper-nickel ores (1 g)	Au, Pd, Pt, Rh, Ir	POLYORGS 4 (3(5)-methylpyrazole groups)	50 ml 1 M HCl or 1 M HNO <sub>3</sub>	0.05 g, bath, 15 min, 130°C, microwave oven, closed vessel	Ashing and residue dissolving with 5 ml of 1 M HCl	ETAAS $n(10^{-6} - 10^{-4})\%$	122
Copper ore, copper concentrate (1–5 g)	Ag, Au, Pd, Pt	Silica gel with <i>N</i> -allyl- <i>N'</i> -propylthiourea groups	200 ml 1 M HCl	0.2 g, 0.5 × 15 cm column, 2 ml min <sup>-1</sup>	Elution by 5 ml of 5% thiourea + 5 ml of 5% thiourea in 1 M HCl	FAAS $10^{-1} - 10^2 \mu\text{g g}^{-1}$	76
Rock, sediment, soil (10 g)	Au	SPHERON-Thiol 1000 mercaptogroups	100 ml 5% HCl	0.1 g, bath, 5 min	Ashing and residue dissolving with 25 ml of NH <sub>4</sub> SCN	ETAAS 0.5 ng g <sup>-1</sup>	133
Road dust (CRM BCR-723), aerosol (0.05 g)	Pd	<i>N,N</i> -diethyl- <i>N'</i> -benzoylthiourea on silica gel	1.86 ml 1–2 M HCl or 1–2 M HNO <sub>3</sub>	0.01 g, on-line, 1 × 13 mm microcolumn, 0.3 ml min <sup>-1</sup>	Elution by 60 µl of ethanol	ETAAS 4 ng g <sup>-1</sup>	31, 81
Geological and metallurgical sample (2 g)	Ag, Au, Pd, Pt	Diphenylthiourea on silica gel	100 ml 1 M HNO <sub>3</sub> (for Pt, 0.2 M HCl)	0.14 g, on-line, 0.3 × 3 cm microcolumn, 5 ml min <sup>-1</sup>	Elution by 5 ml of 2% thiourea in 2 M HCl	FAAS Ag, 0.33; Au, 3.2; Pd, 4.7; Pt, 69 ng ml <sup>-1</sup>	92
Industrial product (0.5 g)	Pt	Thiourea on silica gel	50 ml pH 2.8 (HCl)	0.5 g, on-line, 0.3 × 3 cm microcolumn, 2.5 ml min <sup>-1</sup>	Elution by 10 ml of 2% thiourea, microwave assisted	FAAS 0.06 µg ml <sup>-1</sup>	23
Street dust, anode slime, catalytic converter, rock (0.1–1 g)	Pd	Dimethylglyoxime on silica gel	50 ml pH 4 (HCl)	1 g, 1 × 10 cm column, 2 ml min <sup>-1</sup>	Elution by 10 ml of 1 M HCl in acetone, evaporation and residue dissolving with 5 ml 1 M HCl	FAAS 1.2 µg l <sup>-1</sup> ; ETAAS 0.4 µg l <sup>-1</sup>	86
Road dust, platinum ore (CRM SARM-7) (0.2 g)	Pd	Ammonium pyrrolidine-dithiocarbamate on the fullerene C60	4 ml pH 0.9 (HCl)	0.08 g, 3 × 10 mm column, 0.45 ml min <sup>-1</sup>	Elution by 0.6 ml of ethanol	ETAAS: 0.044 ng ml <sup>-1</sup>	33
Industrial water (50–1000 ml)	Pd	Thiuridazine (thiophenothiazine groups) on silica gel	50–250 ml pH 2.5 (HCl)	0.005 g, Ø47 mm disk 10 ml min <sup>-1</sup>	Elution by 10 ml of 1 M Na <sub>2</sub> SO <sub>3</sub>	FAAS 12 µg l <sup>-1</sup>	87
Catalyst, vegetation, soil, water sample (0.1–0.5 g)	Pt	1,5-Bis(di-2-pyridyl)-methylene thiocarbonylhydrazide (DPTH-gel) on silica gel	100 ml pH 5.0 (HCl + HNO <sub>3</sub> )	0.2 cm, on-line, 0.3 × 3 cm microcolumn, 2.4 ml min <sup>-1</sup>	Elution by 40 µl of 2 M HNO <sub>3</sub>	ETAAS 0.8 ng ml <sup>-1</sup>	32
Environmental sample, catalyst (0.1–0.5 g)	Rh	1,5-Bis(2-pyridyl)sulphonyl methylthio-carbohydrazide (PSTH-gel) on Dowex I-X8	100 ml pH 3.6 (HCl + HNO <sub>3</sub> )	0.2 cm, on-line, microcolumn 0.3 × 3 cm, 2.4 ml min <sup>-1</sup>	Elution by 40 µl of 4 M HNO <sub>3</sub>	ETAAS 0.3 ng ml <sup>-1</sup>	157
Catalyst, synthetic mixture (0.5 g)	Pd	1,5-Diphenyl-carbazone on naphthalene	30 ml pH 1.5 (HNO <sub>3</sub> )	0.15 g, bath, 4–5 min	Elution by 5 ml of 0.25 M thiourea	FAAS 4 µg l <sup>-1</sup>	146
Pharmaceutical (0.1 g)	Pt	2,2'-Diamino-diethylamine on cellulose	20 ml 0.01 M HCl + 0.015% KI	0.04 g, microcolumn, 2 ml min <sup>-1</sup>	Elution by 200 µl of 0.1 M thiourea in 0.5 M HCl	ETAAS 0.1 µg g <sup>-1</sup>	30
Copper ore, concentrate (5–10 g)	Pt	Anion-exchanger Dowex I-V8	200 ml 0.2 M HCl	0.5 g, bath, 30 min	Ashing and residue dissolving with 1 ml of 2 M HCl	ETAAS $n(10^{-1} - 10^{-2})$ µg g <sup>-1</sup>	151
Geological sample (10 g)	Au, Ag, Pd	Activated carbon	200 ml 0.1 M HCl	0.5 g, bath, 4 h	Wet ashing with 20 ml of HNO <sub>3</sub> + 5 ml of HClO <sub>4</sub> , evaporation and residue dissolving with 10 ml of 1 M HCl	FAAS Au, 0.02; Ag, 0.007; Pd, 0.014 µg ml <sup>-1</sup>	141
Environmental sample (0.054 g)	Pt, Pd	Biosorbent (Algae <i>Chlorella vulgaris</i> on Cellex-T)	20 ml pH 1.5–1.8 (HCl)	0.15 g, 3 × 30 mm column, 0.15 ml min <sup>-1</sup>	Elution by 3 ml of 0.3 M thiourea in 1 M HCl	ETTAS 0.2 ng ml <sup>-1</sup>	114

another sensitive line, Au 267.595 nm is overlapped by niobium and scandium (Nb 267.595 and Sc 267.597 nm).<sup>10</sup> Most of the problems can be eliminated by using of spectrometers of the latest generation with semiconductor detectors, which supply analytical information from several lines of each element simultaneously. This allows one to correct for any influence of the sample matrix, so as to avoid systematic errors caused by the self-absorbance of strong lines, as well as to correct for any time instability or drift of the base line.<sup>142</sup> Spectral overlaps that can not be eliminated by a purposeful choice of lines are possible to correct with an instrumental interelement correction.

This approach yields good results if the correction coefficient is less than 10%.<sup>151</sup>

The preconcentration of noble metals allows one to decrease or eliminate matrix and interelement interferences. Sorption preconcentration coupled with ICP-AES ensures the determination of noble metals in a wide variety of industrial and natural objects in the range of  $10^{-4} - 10^{-6}\%$ . Complexing sorbents are mainly used for the preconcentration and ICP-AES determination of noble metals. For the determination of noble metals by ICP-AES after traditional preconcentration techniques (elution, decomposition of sorbent), new ones are also widely



Table 2 Noble metal determination by AES coupled with sorption preconcentration

Sample	Analyte	Sorbent	Preconcentration		Sorbent preparation	Detection limit or range of metal determination	Ref.
			Solution	Mass of sorbent, mode, contact time or flow rate			
Industrial material, coal (0.25 – 1 g)	Au, Pd, Pt, Rh	POLYORGS 17- <i>n</i> (1,3(5)-dimethylpyrazole groups)	100 ml 1 M HCl (for Rh, 1 M HCl + 0.2 M SnCl <sub>2</sub> )	0.16 g, $\phi$ 2.5 cm disk, 0.8 – 1 ml min <sup>-1</sup>	Microwave decomposition with 6 ml of HNO <sub>3</sub> + 2 ml of H <sub>2</sub> O	ICP-AES $n(10^{-6} - 10^{-4})\%$	37, 123, 138
Metal smelter (0.1 g)	Au, Pd, Pt, Ir	Polyacrylacrylaminothiourea chelating fiber	1000 ml 0.01 M HCl	0.1 g, 0.5 × 15 cm column, 20 ml min <sup>-1</sup>	Elution by 15 ml of 4 M HCl + 3% thiourea (at 70°C)	ICP-AES $n(10 - 10^2)$ ng ml <sup>-1</sup>	129
Metal smelter (1 g)	Au, Ru, Pd	Epoxy-imidazole resin	1000 ml pH 4 (HCl)	0.1 g, 0.5 × 13 cm column, 2 ml min <sup>-1</sup>	Elution by 16 ml of 1.25% thiourea in 6 M HCl	ICP-AES $n(10 - 10^2)$ ng ml <sup>-1</sup>	128
Metal smelter (1 g)	Au, Pd, Pt	Epoxy-polyamide chelating resin	100 ml 0.01 M HCl	0.05 g, 0.5 × 12 cm column, 2 ml min <sup>-1</sup>	Elution by 14 ml of 1.25% thiourea in 2 M HCl (50 – 60°C)	ICP-AES $n(10 - 10^2)$ ng ml <sup>-1</sup>	131
Iron rich sediment (1 g)	Au	SRAFION NMRR (thiourea groups)	100 ml 0.1 M HCl	0.01 g, 1 × 5.7 cm column, 1.2 ml min <sup>-1</sup>	Elution by 5 ml of 5% thiourea in 0.66 M HCl	ICP-AES 0.9 ng ml <sup>-1</sup>	1
Pellet catalyst (CRM NIST-2556) (3 g)	Pd, Pt	Metalfix-Chelamine (tetraethylenepentamine groups)	100 ml 0.1 M HCl	0.1 g, on-line, microcolumn, 5 ml min <sup>-1</sup>	Elution by 2 ml of (1 M thiourea + 2 M HClO <sub>4</sub> ) in 4 M HCl	ICP-AES Pt, 22; Pd, 2.5 ng l <sup>-1</sup>	24
Anode slime (0.15 g)	Au, Pd, Pt, Ir	“	250 ml 0.5 M (HCl + HNO <sub>3</sub> = 3:1)	2.5 g, $\phi$ 1 cm column, 2 ml min <sup>-1</sup>	Elution by 10 ml 1 M KCN	ICP-AES Au, 0.5; Pd, 0.8; Pt, 1; Ir, 2 ng ml <sup>-1</sup>	80
Electrolytic bath sample (1 l)	Au, Pd	Chelating resin Duolite GT-73 (thiol groups)	100 ml 0.01 M HCl	1.25 g, 1 × 5 cm column, 0.5 ml min <sup>-1</sup>	Microwave decomposition with 10 ml of H <sub>2</sub> SO <sub>4</sub> + 5 ml of H <sub>2</sub> O <sub>2</sub> , dissolving with 25 ml of H <sub>2</sub> O	ICP-AES Au, 0.085; Pd, 0.28 $\mu$ g l <sup>-1</sup>	137
Environmental sample (3 g)	Pd, Pt	Diphenylthiourea on Amberlite XAD 4	100 ml 5 M HCl + 0.2 M HNO <sub>3</sub>	0.5 g, 0.5 × 5 cm column, 2 ml min <sup>-1</sup>	Elution by 5 ml of 0.4 M thiourea in 1 M HCl	ICP-AES Pt, 18; Pd, 12 ng g <sup>-1</sup>	83
Water sample (50 ml)	Pt	Thiocyanate reagent on polyurethane foam	10 ml 0.01 M HCl	0.05 g, on-line, 3 × 50 mm column, 10 ml min <sup>-1</sup>	Elution by 0.3 ml of 10% HNO <sub>3</sub>	ICP-AES 0.28 $\mu$ g l <sup>-1</sup>	89
Road dust (3 g)	Pt, Pd	Anion-exchanger Dowex 1-X10	100 ml 2.5% HCl + 1.3% HNO <sub>3</sub>	1 g, 1 × 4 cm column, 3 – 4 ml min <sup>-1</sup>	Elution by circulated 4 ml of 0.1% thiourea in 0.1 M HCl (60°C)	ICP-AES 15 ng g <sup>-1</sup>	43
Platinum ore (CRM SARM -7), soil (CRM GBW-07405) (2 g)	Au, Ag, Pd, Pt	Activated carbon	500 ml 0.1 M HCl	1 g, bath, 2 h	Ashing and continuous powder introduction into microwave induced plasma	MIP-AES Au, 43; Ag, 24; Pd, 57; Pt, 550 ng g <sup>-1</sup> (of sorbent)	28

applied. For example, the introduction of a sorbent aerosol in a microwave-induced plasma after dry ashing of the sorbent has been proposed.<sup>28</sup> Examples of noble metal determination in different kinds of materials by ICP-AES after sorption preconcentration are given in Table 2 and in original papers.<sup>24,25,28,43,67,83,89,128,129,137,138,152,153</sup>

### 3.3 Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most promising methods for the determination of noble metal traces due to its low detection limits, efficiency, and multielement determination, as well as its unique capability to measure element isotopic ratios.<sup>154,155</sup> The popularity of ICP-MS is rapidly growing thanks to the development of a market for commercial equipment and considerable price cutting.

For elemental analysis, quadrupole mass-spectrometers are mostly used. As in the case of any instrumental method, ICP-MS is associated with the influence of various factors on the formation of an analytical signal.<sup>156–159</sup> ICP is a unique source where different particles (single-charged and doubly-charged ions, as well as molecular ones) are formed, and the interelement (isobaric) and polyatomic effects are the principle problem of the method. These effects can be caused by either background interferences (argon, water and air components; oxygen, nitrogen), or by the influence of the components of an analyzed sample. Examples of polyatomic interferences at the

noble metal determination are overlap on <sup>195</sup>Pt, originating from <sup>179</sup>Hf<sup>16</sup>O<sup>+</sup>, the effect of <sup>89</sup>Y<sup>16</sup>O<sup>+</sup>, <sup>40</sup>Ar<sup>65</sup>Cu<sup>+</sup>, <sup>35</sup>Cl<sub>3</sub><sup>+</sup> on the determination of <sup>105</sup>Pd, as well as the <sup>206</sup>Pb<sup>2+</sup> and <sup>87</sup>Sr<sup>16</sup>O<sup>+</sup> interferences on <sup>103</sup>Rh, *etc.*<sup>10,158</sup> One of the important tasks in the development of commercially produced mass-spectrometers is an improvement of the correction methods. Thus, to eliminate polyatomic overlaps, reaction/collision cells are proposed.<sup>142</sup> An additional restriction of the method is exacting requirements to the saline composition of analyzed solutions, usually less 0.2%.<sup>2,37</sup>

A search for an optimum way of solution introduction into the plasma is continuing. To improve the nebulization efficiency, alternative introduction techniques, such as electrothermal atomization, ultrasonic nebulization, and thermonebulization are proposed.<sup>10,142</sup> During the determination of extremely low concentrations of noble metals (excluding Au and Rh, possessing one isotope only), an isotope dilution technique is widely applied.

Preconcentration allows one to significantly decrease the probability of mass-spectrum overlappings, and to obtain a solution with a low salt content. Sorption preconcentration techniques have been developed for the following ICP-MS determination of noble metals in various geological and biological materials, catalytic converters and environmental samples. The application of sorption preconcentration coupled with ICP-MS determination of noble metals for

Table 3 Noble metal determination by ICP-MS coupled with sorption preconcentration

Sample	Analyte	Sorbent	Preconcentration		Sorbent preparation	Detection limit or range of metal determination	Ref.
			Solution	Mass of sorbent, mode, contact time or flow rate			
Environmental and geological sample (0.2 g)	Ir	$\alpha$ -Amino pyridine resin	20 ml 0.4 M HCl	0.1 g, 7 $\times$ 50 mm column, 2 ml min <sup>-1</sup>	Dry ashing and residue dissolving with 10 ml of 3% HNO <sub>3</sub>	0.24 ng ml <sup>-1</sup>	26
Platinum ore (CRM SARM-7) (0.25 g)	Au, Pd, Pt, Ir, Rh	Metalfix-Chelamine (tetraethylenepentamine groups)	10 ml 1.2 M HCl	0.5 g, 2 $\times$ 20 cm column, 0.5 – 1 ml min <sup>-1</sup>	Microwave decomposition with 3 ml of conc. HCl + 1 ml of conc. HNO <sub>3</sub> + 2 ml of H <sub>2</sub> O <sub>2</sub> and dissolving to 10 ml with H <sub>2</sub> O	0.15 – 1.2 ng ml <sup>-1</sup>	79
Airborne particulate sample (0.3 – 0.4 g)	Pt	Aliquat 336 on silica gel	25 ml 0.6 M HCl	0.6 g, 9 $\times$ 175 mm column, 0.8 ml min <sup>-1</sup>	Elution by 10 ml of (1 M HCl + 0.1 M HClO <sub>4</sub> )	0.17 ng	127
Rock (CRM PML P-2) (0.2 g)	Ru, Pd, Os, Ir, Pt	TEVA (Aliquat 336 on Amberchrom CG-71)	5 ml 0.1 M HBr	0.1 ml, bath, 24 h	Elution by 2 ml of 6 M HCl + 1.6 ml of (2.2 M HCl–5 M HBr Ru, Pd); 1 ml of 7 M HI (Ir, Pt)	5 pg g <sup>-1</sup>	162
Airborne particulate, engine soot (CRM NIES No. 8) (0.5 g)	Au, Pd, Pt	Septonex on silica gel (N-(1-carbaethoxypentadecyl)trimethylammonium bromide)	50 ml 0.1 M HCl	1 g, 9 $\times$ 20 mm cartridge, 0.8 ml min <sup>-1</sup>	Elution by 10 ml of ethanol, evaporation and dissolving to 25 ml with 0.1 M HCl	Au, 0.09; Pd, 0.05; Pt, 0.1 ng ml <sup>-1</sup>	16, 34
Peridotite (CRM WPR-1, WMS-1), meteorite sample (Orgueil) (0.6 – 1.5 g)	Ru, Pd, Ir, Pt	Anion-exchanger AG 1-X8	50 ml 0.1 M HCl	1 g, 0.8 $\times$ 4 cm column, 1 ml min <sup>-1</sup>	Elution by 6 ml of 5 M HCl + 6 ml of 5 M HClO <sub>4</sub> , evaporation and dissolving with 5 ml of 1% HCl	0.2 – 0.5 ng g <sup>-1</sup>	132
Road dust, soil (0.2 g)	Pt, Pd, Ru, Ir	Anion-exchanger Dowex 1-X8	20 ml ~1.5 M HCl	1.7 g, 0.6 $\times$ 10 cm column, 1 ml min <sup>-1</sup>	Elution by 5 – 10 ml of conc. HNO <sub>3</sub> and dissolving to 20 ml with H <sub>2</sub> O	0.015 – 0.15 ng g <sup>-1</sup>	29
Geological sample (CRM WMG-1, WITS-1) (1 g)	Pt, Pd, Ru, Os, Au, Ag	Anion-exchanger Dowex 1-X8	25 ml 0.4 M HCl	1 g, 7 $\times$ 50 mm column, 2 ml min <sup>-1</sup>	Dry ashing and residue dissolving with 25 ml of 3% HNO <sub>3</sub>	1 pg g <sup>-1</sup>	135
Natural water (30 ml)	Pd	Activated Al <sub>2</sub> O <sub>3</sub>	30 ml pH 1 – 2 (HNO <sub>3</sub> )	0.15 g, on-line 1.6 $\times$ 10 cm column, 3 ml min <sup>-1</sup>	Elution by 300 $\mu$ l of 0.3 M KCN	1 ng l <sup>-1</sup>	164

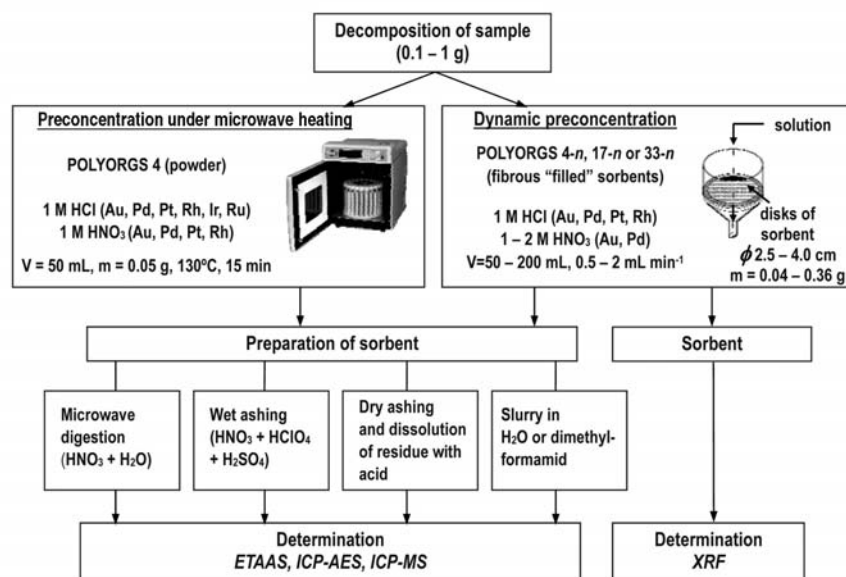


Fig. 1 Scheme of noble metal determination combined with preconcentration by complexing POLYORGS sorbents. POLYORGS 4: fine dispersed complexing sorbent with 3(5)-methylpyrazole functional groups;<sup>54,63</sup> POLYORGS 4-*n*, 17-*n* and 33-*n*: “filled” fibrous materials containing as fillers complexing sorbents with groups of 3(5)-methylpyrazole (POLYORGS 4), 1,3(5)-dimethylpyrazole (POLYORGS 17) and amidoxime and hydrazidine groups (POLYORGS 33) accordingly.<sup>103,165</sup>

different samples is described in Table 3 and in original papers.<sup>30,35,37,44,45,132,135,138,160-164</sup>

Analyses of the features of instrumental techniques show that the use of selective sorbents is preferable for the development of efficient determinations of noble metals. Complexing sorbents ensure the quantitative recovery of noble metals, and the concentrates obtained are free from most impurities, which allows one to enhance the reliability and sensitivity of noble metal detection. An example of using sorption preconcentration as a scheme of noble metal analysis, developed by the authors of this review, is described (Fig. 1). The scheme includes new approaches of noble metal preconcentration by POLYORGS sorbents, as well as sorbent preparation for a subsequent determination of platinum metals and gold by ETAAS, ICP-AES, ICP-MS and XRF. The characteristics of the used sorbents are cited below and in corresponding papers. The scheme has been tested in the analysis of some natural, technological, pharmaceutical samples; satisfactory results were obtained.<sup>37,122,138</sup>

## 4 Conclusions

The literature data show that instrumental methods, mainly ETAAS, ICP-AES and ICP-MS, are widely applied for the determination of trace noble metals in geological, biological, pharmaceutical and environmental samples. To realize the possibilities of the methods, a separation step of these metals from the matrix is necessary. A great number of techniques combined with preliminary sorption preconcentration have been developed. Different types of sorptive materials for noble metals have been synthesized; the most selective are complex-forming sorbents. Along with the sorbents known earlier, the new types, for example, with non-covalently bound complex-forming reagents, are applied. For the preconcentration and elution of noble metals, dynamic (including on-line) systems are preferable. The forms of sorbents used for dynamic preconcentration are various: columns with fine dispersed powders or granules, fibers or "filled" fibrous materials, cellulose filters, etc. To intensify the sorption process and/or decomposition of the sorbent after preconcentration, microwave-assisted techniques have been shown to be efficient.

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