Reviews

Sample Digestion Methods for the Determination of Traces of Precious Metals by Spectrometric Techniques

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Recent advances in digestion methods used in the analysis of precious metal samples by spectrometric techniques are reviewed. The applicability of a fire assay, a wet acid treatment, chlorination and alkaline oxidizing fusion to a quantitative recovery of metals from various materials is discussed. Data on the precious metal contents obtained by using particular digestion methods as well as UV-VIS spectrophotometry, atomic absorption spectrometry, atomic emission spectrometry and inductively coupled plasma mass spectrometry in the examination of various samples are tabulated.

1 Introduction

The members of the platinum group metals (PGM) (ruthenium, rhodium, palladium, osmium, iridium and platinum) and gold are called "precious" or "noble" metals. These names have roots in the unique physical and chemical properties of the metals, owing to their low abundance and high economic value. Precious metals are colored and lustrous, exceptionally stable, hard, malleable, electrically resistant and inert to chemical attacks.

Nobility and catalytic activity are unique properties of precious metals that result in their wide applications, *e.g.* as catalysts in various chemical processes, in electrical and electronic industries, and in jewellery.[1] Growing demand for rhodium, palladium and platinum has resulted from autocatalysts production. Since 1978, platinum complexes, cisplatin and second-generation compounds, have been applied in chemotherapy as effective anticancer drugs.[2] The investigation of ruthenium complexes as an alternative to platinum cancer inhibitors has recently become a subject of extensive studies.

The large variety and complexity of examined materials, wide concentration ranges to be determined (from ng g^{-1} and sub-ng g^{-1} in geological, environmental and clinical samples to % levels in some industrial products), high inertness of noble metals towards many chemical reagents and high chemical similarities of numerous complexes formed make the choice of the analytical methodology for their determination in the sample of interest a challenge. Extensive studies on the methods for the determination of the metals in various matrices with satisfactory

sensitivity, selectivity and reliability have been carried out. Spectrometric techniques, ultra-violet visible (UV-VIS) spectrophotometry, atomic absorption spectrometry (both flame (FAAS) and graphite furnace (GFAAS) techniques), inductively coupled plasma combined with atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS), are widely applied in the analysis of a variety of samples containing noble metals over a large range of concentrations.[3-14]

UV-VIS spectrophotometry was historically the first instrumental technique used for the quantification of small amounts of noble metals in various materials. The technique requires a quantitative conversion of the analytes into stable complexes that can act as the basis of spectrophotometric measurements. The high chemical similarity of noble metals, resulting in the formation of complexes of similar compositions and properties, limits the direct application of UV-VIS spectrophotometry in the analysis of multi-component samples. The developed methods are usually combined with separation procedures.[15] Recent generations of ultra violet-visible spectrophotometers that can operate in the derivative mode or allow direct numerical processing of the absorption spectra of the examined mixtures have substantially extended the possibilities of spectrophotometric methods. Derivative spectrophotometry is a unique technique that allows the elimination of the separation steps that are generally required prior to the detection of the analytes by classical spectrophotometric methods.[16] Success in the application of derivative spectrophotometry requires, however, the simultaneous conversion of the metals into stable complexes. This can cause problems when examining multi-component precious metal samples.

The detection limits (DLs) offered by UV-VIS spectrophotometry make the technique applicable to the

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determination of relatively higher concentrations of the metals (μg g^{-1} levels) as compared with the other spectrometric techniques, *i.e.* AAS, ICP-AES and ICP-MS. The latter techniques can be applied to the determination of trace amounts (ng g^{-1} and sub-ng g^{-1}) of the metals. They have been widely used for the determination of precious metals in a large variety of samples, such as ores, rocks, industrial products, waste solutions and solids, as well as clinical, biological and environmental materials. ICP-MS is particularly suited to the determination of metals in various materials owing to the excellent detection limits (low pg levels), wide dynamic range, possibility of accurate multi-element analysis and unique capability of measuring isotopic ratios.

The direct application of spectrometric techniques to the detection of metals in complex matrices is limited due to numerous interferences, both mutual and those from associated base metals. Interference effects substantially arise in the analysis of non-homogeneous materials when the examination of large samples is required. Much consideration is to be taken for the elimination of interferences, particularly those from common elements present in examined samples, when using the AAS detection technique. The interfering effects of matrix elements may cause problems in the direct determination of precious metals by the ICP-AES technique. Base elements, *e.g.* iron, copper, nickel, chromium, titanium, manganese and vanadium, interfere with the ICP-AES signals of precious metals.[11] Numerous interferences limit the direct application of ICP-MS to the quantification of metals in complex materials. Interferences from ions and polyatomic groups as well as from particular analytes can occur.[4]

Low concentrations of precious metals, particularly in geological and environmental samples, may require preconcentration prior to detection. Volatilization, solvent extraction, coprecipitation, sorption and chromatographic methods are applied to separate precious metals from associated base metals, as well as particular analytes from their mixtures, and to preconcentrate them to the levels detected by the used instrumental technique. An effective combination of the digestion procedure with the separation and detection steps determines the reliability of the results.

The problem of choosing the procedure for the digestion of the examined samples remains a fundamental one in spite of a huge amount of work done to develop accurate methods for the determination of precious metals in various materials. The necessity of examining large samples, the inertness of noble metals to chemical attack and the complexity of their properties in solutions provide large difficulties in the quantitative conversion of the metals into soluble stable complexes. Fire assay (FA), a wet acid treatment, chlorination and oxidation fusion are used for the decomposition of various noble metal samples and for the transformation of the metals into solutions. Recent applications of particular digestion methods in combination with UV-VIS spectrophotometry, AAS, AES and ICP-MS for the examination of various materials are reviewed in this paper.

2 Fire Assay

The FA digestion and preconcentration technique provides the highest recovery of precious metals from a large number of complex matrices, such as ores, rocks, minerals, concentrates and soils. The classical lead assay involves fusion of the examined sample at high temperatures (*ca.* 1100°C) with a flux, namely sodium carbonate (Na_2CO_3), borax ($Na_2B_4O_7$), silica

(SiO_2), lead oxide as a collector (PbO) and a reducing agent (flour, starch).[3,17-23] It results in the extraction of noble metals into a metallic lead button produced by a reaction of PbO with a reducing agent under fusion. The matrix elements react with the flux component to form a slag that is subsequently discarded. The lead button is placed on a cupel prepared from bone ash or magnetite. Upon heating at a temperature of about 800 – 850°C in an oxidizing atmosphere, the lead oxide and the non-noble metal oxides are produced and absorbed into the cupel where upon a bead of precious metals remains. The precious metal bead is treated with acids (HCl, HNO$_3$) to extract the analytes.

The collection of precious metals from large samples (10 – 50 g) of a complex matrix into a relatively small bead of simple metal alloys is the main advantage of the fire assay procedure. Success in the quantitative recovery of precious metals requires, however, an experienced and skilled assayer to optimize both the flux composition and the fusion conditions. High amounts of salts introduced to the sample are disadvantages of the fire assay procedures. They may provide high procedural blanks and difficulties in the direct analysis of the obtained solution by instrumental techniques. Another drawback of the classical fire assay using a lead collector is that it does not provide for an efficient recovery of all noble metals. Quantitative collection can be achieved for gold, silver, platinum and palladium. The technique has found limited applications to the determination of ruthenium, osmium, rhodium and iridium in complex matrices. The recovery of these metals is seriously affected by the flux composition and experimental conditions. Serious losses of ruthenium during the FA procedure were observed.[24] Significant retention of the metal by the slag and the cupel occurred. Losses of osmium due to retention by the slag or the volatilization of OsO$_4$ formed during the cupellation were also reported.[25] Losses of ruthenium in the form of RuO$_4$ during the fusion and cuppelation were negligible.

Modifications to the lead fire assay procedure using silver or gold as collectors for the isolation of PGM from rocks, ores and minerals have been proposed.[26-28] Combining the technique with GFAAS allows the determination of gold, palladium, platinum and rhodium[26] and of platinum, palladium, rhodium and iridium[27] down to ng g^{-1} levels. An alkaline cyanide solution has been used to dissolve noble metals from the silver or gold beads.[26] A successful application of spark-ablation ICP-MS for the direct detection of platinum, palladium, rhodium and iridium in the gold and silver beads was demonstrated.[28]

The application of other iron-nickel-copper,[29] copper,[30,31] tin,[32,33] and NiS[34] fire assay collectors for precious metals has been proposed. Nickel sulfide has been found to be the most effective collector for the quantitative recovery of all precious metals from complex matrices and large samples.[35-51] Recent applications of NiS-FA in chemical speciation studies of PGM in geological samples can be mentioned.[48,50]

The NiS-FA procedure involves fusion of the sample with nickel, sulfur, $Na_2B_4O_7$, Na_2CO_3 and SiO_2 in a clay crucible at a temperature of *ca.* 1000°C. The NiS bead formed is separated from the slag, crushed and then dissolved in hydrochloric acid. The matrix elements are removed under an HCl treatment. The insoluble precious metal sulfides are filtered and dissolved in HNO$_3$ and HCl. A high procedural blank resulting from chemicals required for the flux is the disadvantage of the NiS fire assay method.

The recovery and losses of PGM (μg g^{-1} levels) from ore samples at different stages of the NiS-FA digestion procedure, including optimization of the button size and a dissolution technique, have been examined using ICP-MS detection.[40]

Among the three button sizes investigated, *i.e*., 2.5, 5 and 8 g, the 2.5 g button was found to be adequate for the full recovery of the metals (20 g samples). Losses of the metals, especially of platinum and palladium, during the NiS button dissolution step were minimized by the application of coprecipitation with tellurium. The effect of the collector mass on the recovery of PGM and gold in the analysis of ore ($< \mu$g g^{-1}) and komatiite ($<$ 10 ng g^{-1}) samples by NiS-FA combined with ICP-MS was also investigated.[41]   The recoveries of ruthenium, rhodium, palladium and platinum from komatiite increased along with an increase of the collector mass (0.5 – 5 g of Ni examined). They were independent of the mass of the collector in the analysis of a PGM ore standard reference material (SARM-7).

The use of lithium tetraborate as a flux constituent in FA digestion procedures has been examined.[39]   A lower, as compared with sodium tetraborate, recovery rate (GFAAS detection) from geological standard reference materials, SARM-7, CHR-Pt+ and CHR-Bkg, except for chromitites with PGM abundances in the μg g^{-1} range, has been achieved. Lithium tetraborate was chosen earlier as a preferred reagent for chromium-rich materials, since it improved the dissolution of the chromite grains.[35]

The applicability of the FA technique to the examination of precious metal samples, the fluxing agents, equipment, materials and detection techniques used have been described in detail.[3] Recent FA procedures used in combination with the spectrometric detection techniques in the analysis of various materials are presented in Table 1.

3 Wet Acid Treatment

The digestion of various precious metal samples under a wet acid treatment has been widely examined. The method is simple, fast and inexpensive. Mixtures of HCl, HNO$_3$, HClO$_4$, HF and H$_2$O$_2$ are commonly applied. The ratio of the sample weight to the volume of acids and an appropriate sample mesh size are important factors, particularly in the analysis of complex matrices. Incomplete wetting of the samples, or occlusion of the analytes within the grains, can result in a non-quantitative recovery of the metals. The application of HF is generally required for the complete digestion of geological and more complex environmental materials, *e.g*. dusts, soils and sediments. Hydrofluoric acid attacks the silicate phases and facilitates the liberation of the analytes. The purity of the acids used should be controlled so as to avoid high blank values. Sub-boiling distillation of the commercially available acids can result in the reduction of blanks.

An open-vessel wet acid treatment, high-pressure decomposition systems, microwave heating and a Carius tube technique are incorporated in the digestion procedures. The use of high-pressure systems and microwave heating significantly accelerates the decomposition of the samples and leaching analytes.

The acid extraction effectiveness strongly depends on the chemical solubility of individual metals, their concentration and the kind of matrix. Noble metals exhibit a high resistance to single mineral acids. Palladium and rhodium are the only metals attacked by hot HNO$_3$ and boiling H$_2$SO$_4$, respectively. Aqua regia is used for the dissolution of palladium, platinum and gold.

Recent successful applications of an aqua regia treatment for the determination of gold and palladium in various (geological, anode slime, catalyst and airborne particulate matter) samples by AAS (both flame and graphite furnace) or UV-VIS

spectrophotometry have been presented.[52-58] Mixtures of HCl, HBr and Br$_2$ were also used for the extraction of gold from geological matrices prior to AAS detection.[59]

The high resistance of ruthenium, rhodium, osmium and iridium to an attack by a mixture of acids, including aqua regia, limits the use of a direct wet digestion procedure to their quantitative transformation into soluble species. The metals can be transformed into solution by an aqua regia treatment when accompanying (at low % levels) platinum and paladium[60] or common metals[61] in alloys. Aqua regia is applied for the decomposition of various catalysts containing PGM.[62-68] A decrease in the amounts of nitric acid used is advantageous when determining ruthenium.[69,70] It should be noted, however, that catalysts usually contain small amounts of platinum metals dispersed on the surface of the support, such as alumina, silica, silica-alumina or activated carbon. This significantly facilitates the dissolution of the metals under a wet acid treatment. A non-quantitative recovery of the metals can occur in the analysis of complex materials that may contain them occluded within the grains. There is evidence of a 20 – 40% recovery of platinum, rhodium and osmium, and 1 – 10% of iridium from ores[71] and 55 – 87% of platinum from soils[72] digested by an acid treatment, aqua regia or HF/HClO$_4$ and HNO$_3$/HCl, respectively, followed by ICP-MS detection. Average recoveries of 46 – 55% for platinum, 61 – 78% for gold, 61 – 88% for palladium, 73 – 94% for rhodium, 30% for ruthenium and 44% for iridium by ICP-MS have been reported for ore samples (10 g) digested with aqua regia under heating in a microwave (MW) oven.[73] There are opinions that in the analysis of geological samples a direct aqua regia treatment can be used only for a rapid preliminary evaluation of the precious metals content.[10] Combined digestion procedures, a wet acid treatment followed by alkaline oxidizing fusion of an undissolved residue, are often applied for improving the recovery of the metals.[74-76]

The use of hydrofluoric acid in the digestion procedures is preferable, particularly when examining geological[74,76-85] and environmental materials.[72,86-94] High-pressure systems and microwave heating are widely applied for improving the digestion of such samples. A pressure (PTFE bomb) decomposition method using an HNO$_3$ and HF mixture has been successfully applied in the analysis of manganese crust and geological samples for the content of gold, platinum, palladium and rhodium (ng and pg levels) by GFAAS.[77] HF and HNO$_3$ dissolution followed by an aqua regia treatment in a high-pressure digestion bomb (Paar Instrument Co.) (24 h at 150˚C) has been applied to the determination of ruthenium, rhodium, palladium, iridium and platinum (fg and pg levels) in geological samples (ICP-MS detection).[84] The concentrations of PGM and gold (0.01 – 11.3 μg g^{-1}) in copper-nickel ores, corresponding well with the certified values, were determined by GFAAS using an autoclave decomposition technique along with HCl, HF and HNO$_3$.[82] Hydrofluoric acid and aqua regia have also been used for the digestion of soil matrices when determining palladium at ng levels by GFAAS.[94] Mixtures of HNO$_3$, HF and H$_3$BO$_3$ and a pressure asking device have recently been applied to digest road dust (a candidate reference material) prior to the detection of platinum, palladium and rhodium (ng g^{-1} levels) by various techniques.[91] Samples of 50 – 70 mg were subjected to the digestion procedure. Boric acid was used to solubilize any insoluble fluorides. The application of pressure ashing and various acids (HNO$_3$, HClO$_4$, HF and aqua regia) for the decomposition of dust samples, prior to the determination of platinum by ICP-MS, was examined earlier.[89] The procedure with HNO$_3$, HClO$_4$ and HF was recommended for the analysis of samples containing platinum bound into the silica matrix.

Table 1 Fire assay digestion procedures combined with spectrometric techniques in the analysis of precious metal samples

Sample (weight)	Element determined	Collector/ flux	Separation technique	Detection technique	Concentration	DL	Reference
Concentrate (1 – 50 g)	PGM, Au	Pb	Pb distillation, sorption (Polyorgs IV)	AES	0.059(Os) – 28(Pd) g t^{-1}	ng g^{-1}	18
Products of complex composition (5 – 10 g)	PGM (except Os), Au	Pb	extraction	AAS	0.5 ng g^{-1} – 0.1 μg g^{-1} (Pt, Pd, Rh, Au) 5 ng g^{-1} – 0.1 μg g^{-1} (Ir, Ru)		19
Ores (2.5 g)	Pt, Pd, Rh, Au	Pb/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, SiO$_2$		AES	0.43(Pt) – 30.0(Pd) g t^{-1}	0.1 – 1 μg g^{-1}	20
Geological reference materials	Au, Pd, Pt	Pb		ICP-MS		2(Au), 0.1(Pt), 0.5(Pd) ng g^{-1}	21
CuS concentrates	Ag, Au	PbO/Na$_2$CO$_3$, KNO$_3$, SiO$_2$		FAAS	0.5 – 300(Au), 25 – 1500(Ag) g t^{-1}		22
Urban road dust, soils	Pt	Pb		ICP-MS	0.35 – 32.7 ng g^{-1} <0.30 – 7.99 ng g^{-1}		23
Rocks (SARM-7) (5 – 10 g)	Pd, Pt, Rh	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, SiO$_2$		GFAAS	0.25(Rh) – 5.7(Pt) mg l^{-1}		36
Geological (15 g)	PGM, Au	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, SiO$_2$	Te coprecipit.	ICP-MS		0.5 – 1.26 μg l^{-1}	37
Rocks (SARM-7), chromitite (5 – 15 g)	PGM, Au	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, SiO$_2$	Te coprecipit.	ICP-MS	55(Os) – 3846(Pt); 1.8(Os) – 82.2(Pd) ng g^{-1}	0.09 – 2.1 ng g^{-1}	38
Geological (SARM-7) (20 g)	PGM (except Os)	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, SiO$_2$	Te coprecipit.	ICP-MS	0.07(Ir) – 3.29(Pt) μg g^{-1}	0.5 ng g^{-1}	40
Silicate rocks (5 – 10 g)	Ru, Pd, Ir, Pt	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$	anion-exchange	isotope dilution (ID) ICP-MS	31.3(Ir) – 370(Pt) ng g^{-1}		42
Geological reference materials (1 g)	Ru, Rh, Pd, Ir, Pt, Au	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, SiO$_2$		ICP-MS	0.01 – 1.57 ng g^{-1}		43
Geological reference materials (20 g)	PGM	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$, SiO$_2$	Te coprecipit., OsO$_4$ distillation	ICP-MS		0.01 – 0.39 ng g^{-1}	44
Geological reference materials (15 g)	PGM, Au	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$		laser ablation (LA) high resolution (HR) ICP-MS	6.9(Os) – 249(Pd) ng g^{-1}	0.2(Os, Ir) – 7(Pt) ng g^{-1}	45
Geological reference materials (10 – 15 g)	PGM, Au	NiS/Na$_2$CO$_3$, Li$_2$B$_4$O$_7$		LA ICP-MS		1.7(Au), 3.3(Pd), 8.3(Pt), 1.3(Os), 1(Rh), 5(Ru), 0.7(Ir) ng g^{-1}	46
Rock reference materials (50 g)	PGM, Au	NiS		ICP-MS		1(Rh) – 23(Au) pg g^{-1}	47

Continued

Table 1   continued

Sample (weight)	Element determined	Collector/ flux	Separation technique	Detection technique	Concentration	DL	Reference
Geological	Ru, Rh, Pd, Ir, Pt, Au	NiS	Te coprecipit.	ICP-MS		21(Ru), 3(Rh), 9(Pd), 2(Ir), 13(Pt),53(Au) pg g^{-1}	49
Geological reference materials (10 – 15 g)	PGM, Au	NiS/Na$_2$CO$_3$, Na$_2$B$_4$O$_7$		LA ICP-MS		0.2(Os, Ir) – 7(Pt) ng g^{-1}	51

Recent examples of the successful application of aqua regia alone for the digestion of some environmental materials, such as road dust, soil and urban river sediments (0.20 – 0.25 g samples, high pressure asher (HPA) or microwave heating) for the determination of PGM (ng g^{-1}) by ICP-MS can, however, be mentioned.[95,96] Aqua regia and HF were used to digest airborne particulate matter prior to the detection of platinum, palladium and rhodium (pg m^{-3}) by ICP-MS.[97] A mixture of H$_2$SO$_4$ + CrO$_3$ has been proposed for the decomposition of carbonaceous rocks prior to the determination of PGM by GFAAS.[98]

Highly efficient acid (HNO$_3$, HCl) digestion procedures for various types of rocks including silicates and sulfides (0.1 – 5 g samples) have been developed using a Carius tube design.[99-102] In the Carius design, an acid treatment is accomplished in a sealed thick-walled Pyrex tube at high temperature (240°C) and elevated pressure for ~12 h.[99] High efficiency in leaching analytes and low procedural blanks have been achieved. A modified Carius design incorporating a liner of high-purity quartz glass inside the outer borosilicate shell allowed a reduction of the blank values by a factor of 10 – 100, as compared with the standard NiS-FA sample-preparation technique.[101] A preliminary desilification procedure with HF is usually added to the sample-preparation step for examining materials with silicate matrices.

The Carius tube method has been found to be particularly suitable for the complete recovery of osmium which is easily oxidized to volatile OsO$_4$.[99,100] A comparison of the conventional Teflon vessel and the Carius tube digestions of various types of rocks, including silicates, sulfides and metals showed that the latter technique liberates more osmium from most matrices and is more robust for measuring the isotopic composition of the samples. Recently, >80% recovery of osmium (µg g^{-1} levels, ICP-MS detection) from iron meteorites, using the atmospheric pressure apparatus and a longer by a factor 10 decomposition time, has been achieved.[103] The Carius tube dissolution provided better results for platinum, palladium and rhodium by 0.16%, 0.43% and 1.00%, respectively in the used autocatalysts, as compared with hot-plate dissolution (HNO$_3$, HClO$_4$ and HF).[104] A comparison of a high-pressure asher and Carius tube technique for the digestion of chromitites and other geological materials prior to the detection of ruthenium, palladium, rhenium, osmium, iridium and platinum (ng g^{-1} levels) by ICP-MS has recently been presented.[105] A higher temperature (320°C) than that which can be reached in HPA has been considered to be the advantage of the technique.

The wet acid treatment (HNO$_3$, HNO$_3$ and HCl, HNO$_3$ and HClO$_4$, HNO$_3$ and H$_2$O$_2$) has been successfully applied to the total digestion of clinical as well as some biological materials. Until now, the determination of ultra-traces of platinum has been the subject of most studies.[106-116] The direct digestion in HNO$_3$ (borosilicate tubes, *ca.* 100°C) had been used prior to the detection of platinum in blood, urine and tissue speciments by ICP-MS (DL of 0.1 µg l^{-1}) and GFAAS (DL of 10 µg l^{-1}).[106] Samples of tissue[107] and cell cultures exposed to cisplatin[109] were prepared for analysis by HPLC ICP-AES or ICP-MS by dissolving in HNO$_3$, followed dry ashing at 450°C, or direct digestion in HNO$_3$ (2 h heating at 70°C), respectively. Mixtures of HNO$_3$ and HCl have been used for the digestion of tobacco and bean samples (high-pressure PTFE bombs),[108] and tree bark (MW heating)[115] prior to the detection of platinum by GFAAS (DL of 0.3 ng Pt) and ICP-MS (double focusing, DL of 0.03 ng g^{-1}; quadrupole, DL of 0.2 ng g^{-1}), respectively. Digestion in HClO$_4$ and HNO$_3$ preceded the determination of platinum in cisplatin and carboplatin by HPLC,[110] in plant tissue[111] and in mouse liver and corn leaves[112] by the ICP-MS technique. Microwave digestion procedures using HNO$_3$ and H$_2$O$_2$ have been developed for the determination of platinum in wine (GFAAS)[114] as well as fish liver and mussel soft tissue (ICP-MS).[116] The results for the platinum content in wine were in agreement with those obtained using dry mineralization. Rhodium in biological materials (bovine liver, non-fat milk powder and oyster tissue) has been determined by GFAAS (DL of 16.5 ng ml^{-1}) after digestion with HNO$_3$ and H$_2$O$_2$ (120°C, 3 h).[117] Ultra-violet photolysis has been proposed for the determination of physiological levels of palladium, platinum, iridium and gold in human blood[118] and palladium and platinum in urine[119] to minimize the amounts of the reagents (HNO$_3$, H$_2$O$_2$) used in the digestion procedures. The application of microwave and ultrasonic HNO$_3$, H$_2$O$_2$ digestion procedures for the transformation of palladium and platinum from airborne dust collected on glass fiber filters[120,121] and platinum from tunnel dust[122] into solutions has been reported.

Only dilution with acids was satisfactory prior to the detection of platinum and ruthenium in biological fluids by ETAAS.[123-125] Samples of human plasma, ultrafiltrate plasma, saliva and urine have been diluted with 0.2 M HCl + 0.15 M NaCl[123] or 0.2% HNO$_3$ +0.1% Triton X-100.[124] Dilution with water has been used in the determination of platinum in urine and plasma by the ICP-AES technique.[107]

The examples of wet acid digestion procedures recently developed for the analysis of various precious metal samples using spectrometric detection techniques are presented in Table 2.

4 Chlorination

Platinum group metals and gold undergo a chlorine attack,

Table 2 Wet acid digestion procedures for precious metal samples examined by spectrometric techniques

Sample (weight)	Element determined	Dissolution	Separation technique	Detection technique	Concentration	DL	Reference
Ore (1 – 10 g)	Au	aqua regia	extraction	FAAS	0.45 – 1.07 g t^{-1}		52
Anode slime (50 – 100 mg)	Au, Pd	aqua regia	anion-exchange	UV-VIS spectrophot.	996(Au) – 3.7(Pt) μg g^{-1}		53
Ore (2 g)	Au	aqua regia	chelation chromatogr.	GFAAS		0.65 μg l^{-1}	54
Geological (0.5 g)	Au, Pd	aqua regia	chelation chromatogr.	GFAAS		20(Au) – 0.35(Pd) ng ml^{-1}	55
Geological (1 g) anode slime (0.1 g)	Au	aqua regia	anion-exchange	FAAS	7.23 μg g^{-1} 0.071%	46 μg l^{-1}	56
Airborne particulate matter (filter)	Pd	aqua regia	chelation chromatogr.	GFAAS	0.2 – 14.6 pg m^{-3}		57
Ore, catalyst (2 – 5 g)	Pd	aqua regia		UV-VIS spectrophot.	193 – 503 μg g^{-1}	0.07 μg ml^{-1}	58
Cu alloys (0.2 – 15 mg)	PGM	aqua regia		GFAAS	1.5×10^{-4} – 0.03%		61
Catalysts (3 g)	Pt, Ir	aqua regia		UV-VIS derivative spectrophot.	0.3(Pt) – 0.2(Ir)%		62
Co$_3$O$_4$ catalysts (2 g)	Pt, Rh	aqua regia (followed H$_2$ reduction)	Pt extraction	FAAS	$(2.07 – 2.54) \times 10^{-2}$(Rh), $(1.10 – 1.63) \times 10^{-2}$(Pt)%		63
Catalyst (0.1 g)	Pt	aqua regia		UV-VIS spectrophot.	35.20 – 35.50 μg		64
Pt/C catalyst (50 mg)	Pt, Pd, Rh	aqua regia/ NaOH fusion		FAAS		3(Pd) – 40(Rh) μg l^{-1}	66
Autocatalyst (0.5 – 1 g)	Pd, Pt	aqua regia		UV-VIS derivative spectrophot.	0.0102(Pd) 0.207(Pt)%		67
Pt-Sn/MgO catalyst (20 – 30 mg)	Pt	HCl, aqua regia (MW)		ETAAS	18.5 – 19.8 mg g^{-1}		68
Pt/C, Pt-Ru/C catalysts (2 – 20 mg)	Pt, Pt, Ru	aqua regia, HCl + HNO$_3$ (6 + 1)		UV-VIS derivative spectrophot.	16.7(Pt); 22.2(Pt), 3.4(Ru)%		69
Pt-Ru-Ge catalyst (5 – 17 mg)	Ru	HCl + HNO$_3$ (6 + 1)		UV-VIS spectrophot.	0.49%		70
Geological (chromitite, silicates) (10 g)	PGM, Au	aqua regia		ICP-MS	6010(Pd) – 2(Rh) μg kg^{-1}		71

Continued

Table 2   continued

Sample (weight)	Element determined	Dissolution	Separation technique	Detection technique	Concentration	DL	Reference
Soil (2 g)	Pt	HF, $HClO_4$ HNO_3, HCl	Te coprecipit.	ID ICP-MS	3.77 – 4.05 ng g^{-1}	0.08 ng g^{-1}	72
Ore (10 g)	PGM, Au	aqua regia (MW)		ICP-MS			73
Ores, concentrates, mattes, silicate and iron-formation rocks (2 – 5 g)	PGM (except Os)	HF, aqua regia/Na_2O_2 fusion	cation-exchange or Te coprecipit.	GFAAS	µg g^{-1}, ng g^{-1}		74
Geological (1 g)	Ru, Rh, Ir, Pt	aqua regia (MW)/Na_2O_2 fusion	cation-exchange	ICP-MS		1.3(Rh) – 11(Pd) ng g^{-1}	75
Ores, rocks (SARM-7) (0.25 g)	Au, Pt, Pd, Ir, Rh	aqua regia, HF/Na_2O_2 fusion	ion-exchange	ICP-MS		0.5(Rh) – 4.0(Au) ng g^{-1}	76
Geological (0.5 – 1.5 g)	Au, Pt, Pd, Rh	HNO_3, HF (PTFE bomb)	Se coprecipit.	GFAAS	ng – pg levels		77
Geological (SARM-7) (0.5, 5 g)	Au, Pd, Pt, Rh	aqua regia, HF	Hg coprecipit.	GFAAS	227(Rh) – 1580 (Pt) ng g^{-1}	0.3(Au) – 0.5(Pd) ng kg^{-1}	78
Copper concentrate (5 g)	Au	HCl, H_2O_2, HNO_3, HF	reductive coprecipit.	FAAS, ICP-AES	2 – 20 µg g^{-1}	0.1 µg g^{-1}	79
Silicate rocks, ores, metallurgical samples (5 g)	PGM, Au	HF, aqua regia	cation-exchange	GFAAS	µg g^{-1}, ng g^{-1}	3.7 pg(Au) – 80 pg(Pt)	80
Ore (0.5 – 1 g)	Au	HNO_3, $HClO_4$, HF, aqua regia	sorption	FAAS			81
Cu-Ni ores (1 – 5 g)	PGM, Au	HCl, HF, HNO_3	extraction	GFAAS	0.01(Ru) – 11.3(Pd) µg g^{-1}	0.001(Au) – 0.06(Os) µg g^{-1}	82
Rocks, ores (2 g)	Au, Pt, Pd	aqua regia, Br_2, HF, Rh		ICP-MS		0.01 – 0.06 ng ml^{-1}	83
Geological	Ru, Rh, Pd, Ir, Pt	HF, HNO_3, aqua regia (Paar bomb)	cation-exchange	ICP-MS		fg, pg levels	84
Sulfide ore (5 – 10 g)	Rh, Pd, Pt	HNO_3, HCl, HF/Na_2O_2 fusion	solid phase extraction	FAAS	2.0 – 5.1(Rh), 5.8 – 6.3(Pd), 1.1 – 2.5(Pt) µg g^{-1}	3 – 8 ng g^{-1}	85
Cu alloys (2 – 5 g)		aqua regia			70 – 240(Rh), 1000 – 2800(Pd), 310 – 900(Pt) µg g^{-1}		
Sediments (0.5 – 1 g), nodules, organisms (3 – 5 g)	Pt, Ir	HNO_3, $HClO_4$, HNO_3, HF/Na_2O_2 fusion	anion-exchange	GFAAS	0.01 – 1(Pt) 0.0009 – 7.4(Ir) ng g^{-1}		86
Airborne particulate matter (1.5 g)	Pt	HF, $HClO_4$, aqua regia	cation-exchange	ICP-MS	0.014 – 0.184 µg g^{-1}	0.005 µg g^{-1}	87

Table 2   continued

Sample (weight)	Element determined	Dissolution	Separation technique	Detection technique	Concentration	DL	Reference
Plants (0.25 g)	Au	aqua regia, HF		ICP-MS		0.04 ng ml^{-1}	88
Dust (0.1 – 1 g)	Pt	aqua regia, HNO$_3$, HClO$_4$, HF		ICP-MS	67.9 – 68.2 ng g^{-1}	0.5 – 10 ng l^{-1}	89
Airborne particulate matter (filter)	Pd, Pt, Rh	aqua regia, HF (MW)		HR ICP-MS	21.2 – 85.7(Pd), 7.8 – 38.8(Pt), 2.2 – 5.8(Rh) pg m^{-3}	0.2(Rh) – 1.0(Pd) pg m^{-3}	92
Road dust (100 mg)					102 – 504(Pd), 14.4 – 62.2(Pt), 1.9 – 11.1(Rh) ng g^{-1}	0.5(Rh) – 2.5(Pd) ng g^{-1}	
Road dust (100 mg)	Rh, Pd, Pt	HNO$_3$, HCl, HF (MW)		HR ICP-MS	9(Rh), 17(Pd), 63(Pt) ng g^{-1}	0.1(Rh), 0.5(Pd), 0.4(Pt) ng g^{-1}	93
Soil (5 g)	Pd	aqua regia, HF	solvent extraction	GFAAS	7.2 – 58.6 ng g^{-1}		94
Road dust, soil (0.2 g)	Pt, Pd, Ru, Ir	aqua regia (HPA)	anion-exchange	ID ICP-MS	0.16(Ir) – 47(Pt) 0.1(Ir) – 87(Pt) ng g^{-1}	0.15(Pt), 0.075(Pd), 0.015(Ru, Ir) ng g^{-1}	95
Sediments (0.25 g)	Rh, Pd, Pt	aqua regia (MW)		HR ICP-MS	0.67(Rh) – 472(Pd) ng g^{-1}	0.6(Rh) – 7.8(Pd) ng l^{-1}	96
Airborne particulate matter (filter)	Pt, Pd, Rh	aqua regia, HF (MW)		ICP-MS	n.d. – 9.3(Rh) 3.0 – 15.5(Pt) pg m^{-3}	0.6(Pt), 3.3(Pd), 0.9(Rh) ng l^{-1}	97
Carbonaceous rocks (1 g)	Au, Pt, Pd, Rh, Ir, Ru	H$_2$SO$_4$, CrO$_3$		GFAAS ICP-AES			98
Rocks (silicates, sulfides), metals (0.1 – 5 g)	Os	aqua regia (Carius tube)	distillation	MS	ng g^{-1}		99
Geological (5 g)	Ru, Pd, Ir, Pt	HCl, HNO$_3$ (Carius tube)	ion-exchange	ID ICP-MS		1 – 15 pg g^{-1}	101
Komatiite reference material	Pd, Ir, Ru, Re, Os, Pt,	acids (Carius tube)	solvent extraction and ion-exchange	ICP-MS		3(Os, Ir) – 15(Pt) pg g^{-1}	102
Iron meteorites (0.1 – 2 g)	Os	HCl (atmospheric pressure)		ID ICP-MS	0.02 – 50 µg g^{-1}		103
Autocatalysts (0.1 g)	Pt, Pd, Rh, Pb	HCl, HNO$_3$, (Carius tube) (HF)		ICP-MS	697.4, 1131(Pt), 326, 233.2(Pd), 51.2, 135.1(Rh) µg g^{-1}		104
Geological (2 g)	Ru, Pd, Re, Os, Ir, Pt	HCl, HNO$_3$ (HPA)	anion-exchange	ID ICP-MS	0.15(Ir) – 70(Pd) ng g^{-1}	0.012(Re, Os) – 0.77(Pt) ng	105
Blood, plasma (0.5 – 2 ml), tissue (1 g)	Pt	HNO$_3$		ICP-MS GFAAS		0.1 µg g^{-1} 0.2 – 10 µg g^{-1}	106

Continued

Table 2   continued

Sample (weight)	Element determined	Dissolution	Separation technique	Detection technique	Concentration	DL	Reference
Tobacco, beans, slag, dust (0.1 – 2 g)	Pt	HNO_3, HCl (PTFE bomb)	electro-deposition	GFAAS	2.6 0.12 – 0.55 0.050 0.012 $\mu g\ g^{-1}$	0.3 ng	108
Cisplatin, carboplatin	Pt	$HClO_4$, HNO_3	HPLC		0.02 – 2.5 $\mu g\ ml^{-1}$	0.11 ng	110
Urine, plants, soil, dust (0.1 g)	Pt	HNO_3, $HClO_4$ HNO_3, $HClO_4$, HF	adsorption chromatogr.	ICP-MS		1 pg	111
Mouse liver, (100 mg) corn leaves (50 mg)	Pt	HNO_3, $HClO_4$, aqua regia		ICP-MS	180 ng g^{-1} – 2.8 $\mu g\ g^{-1}$	8 – 25 ng l^{-1}	112
Mice tumor tissue (0.1 g)	Pt	HNO_3		GFAAS	30 – 1000 $\mu g\ l^{-1}$	3 $\mu g\ l^{-1}$	113
Wine	Pt	HNO_3, H_2O_2 (MW)		GFAAS		100 pg Pt	114
Tree bark (0.5 g)	Pt	HNO_3, HCl (MW)		ICP-MS	0.07 – 5.4 ng g^{-1}	0.03 – 0.2 ng g^{-1}	115
Fish liver, mussel tissue (300 mg)	Pt	HNO_3, H_2O_2 (MW)		ICP-MS	0.1 – 2.3 ng g^{-1}	0.2 ng g^{-1}	116
Bovine liver, non-fat milk, oyster tissue (1 g)	Rh	HNO_3, H_2O_2		GFAAS		16.5 ng ml^{-1}	117
Airborne dust (filter)	Pd, Pt	HNO_3, H_2O_2 (MW)	electro-deposition	GFAAS	0.023 – 0.08(Pd) 0.27(Pt) $\mu g\ l^{-1}$		120
Airborne porticulate matter (filter), automobile catalyst (0.5 g)	Pd	HNO_3, H_2O_2 (ultrasonic bath)	extraction	UV-VIS spectrophot.	0.077 – 19.6 $\mu g\ g^{-1}$	0.007 mg l^{-1}	121
Tunnel dust (0.3 – 0.4 g)	Pt	HNO_3, H_2O_2 (MW)	anion-exchange	ICP-MS	13.1 ng g^{-1}	0.17 ng g^{-1}	122
Autocatalysts (0.05 – 0.25 g)	Pt, Pd, Rh	HNO_3, HF, HCl, or H_2SO_4, H_3PO_4, aqua regia		ICP-MS	2250(Pt) – 7.4(Pd) $\mu g\ g^{-1}$	0.0015(Rh) 0.012(Pt) 0.26(Pd) $\mu g\ l^{-1}$	126
Car exhaust fumes (filter)	Pt, Rh, Pd	HNO_3, HF, HCl (MW)		ICP-MS	ng km^{-1}		127
Automobile catalyst (0.1 g)	Pd	HF, HCl		UV-VIS spectrophot.	0.96 – 1.96 mg g^{-1}		128

yielding binary chlorides and salts, both dissolved in weak hydrochloric acid.[4,10,129,130]   The chlorination products can be separated from resistant and water-insoluble components of the examined samples by filtration.   The detection of the metals by selective spectrometric techniques can be accomplished directly in the obtained solutions without any further chemical treatment.

Three types of chlorination procedure are used: "direct"

Table 3 Chlorination procedures in combination with spectrometric detection in the analysis of precious metal samples

Sample (weight)	Element determined	Chlorination agent	Temp. (time)	Dissolution	Detection technique	Concentration	Reference
Rocks (25 g)	PGM, Au	NaCl, Cl$_2$	580°C (3.5 h)	10% HCl	ICP-MS	0.7 – 37 ng g^{-1}	129
Rock pulp (250 g)	PGM, Au	NaCl, Cl$_2$	580°C (3.5 h)	10% HCl	ICP-MS	ng g^{-1}	130
Sulfide concentrates, metal coated glass wool (1 g)	PGM, Au	NaCl, Cl$_2$	500 – 600°C (1.5 h)		AES, AAS	95 ng g^{-1} – 2.78% (Pt, Pd, Rh)	131
Metallurgical samples (0.1 – 2 g) (50 mg)		HCl + KMnO$_4$ / CCl$_4$, CuCl$_2$	160°C (2 – 3 h) / 800°C (2 h)		AAS, ICP-AES	5 × 10^{-5}(Rh) – 30.09(Pd)%	132
Ore (0.1 – 0.3 g)	PGM	HCl, Cl$_2$	250°C (10 h)	2 M HCl	FAAS	0.072(Ru) – 85.8(Pt)%	133
Catalyst (2 g)	Ru	Cl$_2$	750°C (6 h)	HCl	UV-VIS spectrophot.	0.350 – 0.367%	134

chlorination in the presence of large amounts of alkali chloride, "wet" chlorination at elevated temperatures and pressures in a sealed tube containing HCl and an oxidizing agent, and "dry" chlorination by hot chlorine passing over a sample usually mixed with a small amount of NaCl in an open tube at 500 – 600°C. Dry chlorination has such advantages as large samples (up to 25 – 250 g) that can be submitted for analysis, low concentration of salts and low blank levels (less than 0.1 ng g^{-1} for most of the elements).

Recoveries >90% of nanogram amounts of PGM and gold occurring in the form of native metals, natural alloys and sulfide minerals in rock pulps were achieved by dry chlorination combined with ICP-MS.[129,130] The examination of reference rock pulps showed that the results obtained by the dry chlorination method are comparable to, or even better than, those from the fire assay technique.

Direct chlorination was earlier considered to be a promising method for the analysis of a variety of complex commercial samples, including automotive catalysts, using AES and AAS.[131] Chlorination in two closed system: (in autoclaves with a mixture of HCl and KMnO$_4$ (0.1 – 2 g samples) or in sealed silica ampoules with carbon tetrachloride (or CuCl$_2$) (50 mg samples)) has been applied for the decomposition of metallurgical samples (copper-nickel-sulfide ores, slages and platinoid concentrates) and a subsequent determination of PGM (μg g^{-1} – % levels) by AAS or ICP-AES.[132] No losses of ruthenium and osmium from ore samples submitted to chlorination in sealed ampoules (250°C, 10 h) have been observed.[133] A combination of chlorination (in Cl$_2$ stream) with UV-VIS spectrophotometry has been used for the determination of ruthenium at % levels in a spent catalyst.[134]

The chlorination procedures used for the determination of precious metals in various samples are summarized in Table 3.

5 Oxidizing Fusion

Precious metals are readily attacked by alkaline hydroxides in the presence of an oxidizing agent, such as alkali metal peroxide or nitrate. Sodium hydroxide mixed with sodium peroxide, or sodium peroxide alone, are most frequently used as a flux. Fusion operation is usually performed at 450 – 600°C for 15 – 60 min. The melt is dissolved in water and acidified with hydrochloric acid for converting the analytes into chloro-complexes, which serve as the basis of most separation and determination methods. Large amounts of salts and contaminations introduced to the sample, including those from the wall of the crucible attacked by the flux, are the disadvantages of fusion procedures. The application of the method is restricted to small sample weights (0.5 – 2 g).

Silver crucibles are often applied in fusion procedures. Silver that partially passes into the melt during the fusion operation can be quantitatively removed in the form of AgCl after acidifying the melt with HCl. A nickel crucible can also be used. The application of glassy carbon crucibles in the geological sample fusion procedures has been reported.[135] In order to protect the crucible from an attack by the sodium peroxide flux, a layer of sodium carbonate was applied to line the bottom and walls of the crucible before fusion.

Alkaline oxidizing fusion is an effective way for the dissolution of ruthenium, osmium, rhodium and iridium, which are metals having a high resistance to acid attack. The method is widely used to prepare ruthenium standard solutions. Metallic powder ruthenium is completely oxidized to soluble sodium ruthenate, Na$_2$RuO$_4$, under a treatment with a mixture of NaOH + Na$_2$O$_2$ at 450 – 600°C.[136] Stable RuOHCl$_5^{2-}$ and Ru$_2$OCl$_{10}^{4-}$ complexes are formed after acidifying the obtained ruthenate solution with hydrochloric acid.[137,138]

Fusion with sodium peroxide was successfully used to decompose various geological samples containing ruthenium, rhodium, palladium, iridium, platinum and gold.[135,139-142] The detection of the metals by GFAAS or ICP-MS techniques has been preceded by separation with tellurium coprecipitation[135,141] or by anion-exchange chromatography.[139,140,142] The latter method requires a quantitative transformation of compounds occurring in alkaline media into defined, stable anionic chloro-

Table 4   Oxidizing fusion of precious metal samples prior to spectrometric detection

Sample (weight)	Element determined	Flux	Temp. (time)	Separation technique	Detection technique	Concentration	DL	Reference
Geological (0.5 g)	Pt, Pd, Ru, Ir	Na_2O_2	200˚C (15 min) 490˚C (1 h)	Te coprecipit.	ICP-MS	0.15(Ir) – 3792(Pt) ng g^{-1}	0.3 – 2 ng g^{-1}	135
Ruthenium oxide (RuO_2), ruthenites (30 – 60 mg)	Ru	NaOH	dull-red heat (15 min)		UV-VIS differential spectrophot.	75.95% (RuO_2) 27.1 – 28.3% (ruthenites)		136
Silicate rocks (SARM-7) (0.5 g)	Pt, Pd, Au	Na_2O_2	550 – 600˚C (1 h)	anion-exchange	GFAAS	µg g^{-1}		139
Rock (0.6 – 1.5 g) meteorite (60 mg)	Ru, Pd, Ir, Pt	Na_2O_2, NaOH	600˚C (30 min)	anion-exchange	ICP-MS	6 – 10 ng	0.2 – 0.5 ng g^{-1}	140
Geological (1 – 20 g)	Ru, Rh, Pd, Ir, Pt, Au	Na_2O_2	700˚C (10 min)	Te coprecipit.	ICP-MS	ng g^{-1}	1 – 9 pg g^{-1}	141
Impact breccias (1 g)	PGM	Na_2O_2	650˚C (30 min)	anion-exchange	ICP-MS	ng g^{-1}		142
Cu-Ni concentrates (0.5 – 2 g)	Os	Na_2O_2, NaOH		extraction	GFAAS	0.07 – 0.5 gt^{-1}		143
Secondary raw materials (Au-Ag-Cu) (0.1 – 0.5 g)	Au	Na_2O_2	800˚C (20 min)		ICP-AES	58.80%		145
Metallurgical samples (0.5 g)	Pt	Na_2CO_3, Na_2O_2	700˚C (10 min)	sorption	FAAS	1.21 – 303 µg g^{-1}		146

complexes that can be used in separation procedures. The formation of hydroxochloro-complexes on acidification with HCl provided low and variable results for the content of platinum and gold, of 46% and 76%, respectively, in the analysis of silicate rocks.[139] The percolation of chlorine gas through the sample solution was applied to improve the conversion of PGM into chloro-complexes of high affinity to anionic resin.[142]

Alkaline (Na_2O_2, NaOH) fusion has been used to digest copper-nickel concentrates prior to the determination of osmium.[143] The extraction separation of osmium prior to the detection by GFAAS has been applied. Earlier experiments showed that metallic osmium could be quantitatively transformed into a soluble osmate by fusion with NaOH.[136] The low stability of osmate solutions limits the application of the technique in the analysis of real samples.

Alkaline oxidizing fusion is often combined with a wet acid treatment for the decomposition of acid resistant components of the examined materials.[74-76] Any residue not dissolved in acids is submitted to Na_2O_2 fusion and, after dissolution, is combined with the main sample. The application of the sodium peroxide fusion procedure for the preparation of an automobile catalyst for the determination of platinum, palladium and rhodium by ICP-MS has recently been examined.[144] The method provided 100% recoveries of all metals. It was recommended as an alternative to the fire assay sample digestion method.

Oxidizing fusion procedures combined with spectrometric

techniques in the examination of various precious metal samples are presented in Table 4.

The application of fluorooxidants, such as liquid bromine fluoride (BrF_3) and molten potassium tetrafluorobromate ($KBrF_4$), for the dissolution of precious metals has recently been extensively examined by Mit'kin and co-workers.[147-152] The method is based on the treatment of samples (e.g. ores, concentrates, process materials) having an appropriate volume with liquid BF_3 with a subsequent transformation of fluoro-complexes formed into chlorides under HCl action. Quartz or glassy carbon crucibles are used in the decomposition procedures. The insoluble residue is decomposed by a treatment with excess $KBrF_4$ at 350 – 400˚C for 2 – 4 h with subsequent processing using 2 – 4 M HCl. An oxygen stream at 650 – 700˚C can also be used for the oxidation of an insoluble residue after a BrF_3 treatment of the samples. The possibility to minimize the losses of PGM organometallic compounds due to volatilization by the use of fluorooxidants in the decomposition step has been demonstrated.[148] The applicability of oxidizing fluorination with BrF_3 and alkaline fusion with NaOH, Na_2O_2 and Na_2CO_3 to the determination of ultra-low levels of gold and PGM (AAS detection) in resistant geochemical materials, including chromites, molybdenites and ultrabasic ores, has recently been considered.[153]

6 Conclusions

The effect of the sample-preparation steps on the quality of the analytical results is universally recognized. The application of an appropriate digestion procedure and its effective combination with the separation and detection methods are of major importance in the analysis of precious metal samples. The high tendency of PGM and gold to form a heterogeneous distribution, the low concentrations to be determined in a variety of matrices and numerous interferences seriously limit the direct application of even highly sensitive and selective spectrometric techniques, *e.g.* ICP-MS, to the examination of samples. Complete digestion of the examined materials and a quantitative transformation of the analytes into stable soluble complexes that can make the basis of separation, preconcentration and detection steps are required for ensuring a quantitative recovery of the metals. The necessity of examining large samples, the inertness of noble metals to chemical attack and the complexity of species formed make the quantitative digestion of samples particularly difficult and generate major uncertainties in the final analytical results. The possibility of elevating the quality of the results is drastically limited by a lack of certified reference materials. This problem is of great importance in the analysis of environmental samples containing PGM at extremely low concentrations (ng and pg levels). The examination of samples by various methods and interlaboratory studies are strongly recommended.

The FA using an NiS collector has been found to be the most effective digestion technique for the quantitative recovery of precious metals from complex matrices and large samples. Major precautions to lower the level of contaminations from the flux components are necessary.   An examination of the solutions obtained from any partial dissolution of an NiS button for precious metal contents is recommended.

The application of a wet acid treatment, widely used for the decomposition of many materials containing palladium, platinum and gold, is limited when determining the other elements, *i.e.* ruthenium, rhodium, osmium and iridium. Ruthenium, rhodium, osmium and iridium resist a mineral acid treatment, including aqua regia. The effectiveness to transform the metals into soluble complexes strongly depends on the concentration levels, the kind of matrix and the conditions used. The decomposition of silicates under a hydrofluoric acid treatment is generally required for releasing the precious metals occluded within the grains. The application of high-pressure systems and microwave heating may substantially improve the digestion of complex materials and leaching analytes.

Direct chlorination is considered to be a very effective method for the complete recovery of precious metals from geological samples. Large samples that can be submitted for analysis and low procedural blanks are the advantages of chlorination procedures. The necessity to build a special apparatus for the decomposition of samples is probably a reason for the relatively rare applications of the technique.

The use of alkaline oxidation fusion, a method of high effectiveness in the dissolution the metals resisting a wet acid treatment, is limited to the examination of small samples. A high concentration of salts introduced to a sample and low stability of the species formed are the disadvantages of fusion procedures.

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