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Review

Determination of rhodium: Since the origins until today Atomic absorption spectrometry

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Abstract

Rhodium is present at about 0.001 ppm in the earths crust. Rhodium metal is known for its stability in corrosive environments, physical beauty and unique physical and chemical properties. Recent interest in the medical and industrial significance of platinum and to a lesser extent palladium and rhodium has been accompanied by an increasing interest in their determination at low levels.

Platinum group elements (PGEs: Pt, Pd, Rh, Ru, Ir and Os) play a decisive role in the performance of catalytic converters, world-wide applied in vehicles and in some household utensils, to reduce the emission of gaseous pollutants, such as carbon monoxide, nitrogen oxides and hydrocarbons. Since then, approximately 73% of the world production of rhodium is consumed in the production of autocatalyst. However, the hot exhaust gases flowing through the converter cause abrasion of these units, leading to the emission of these elements to the environment. The concentration level of rhodium (also platinum and palladium) is still very low in the nature; accordingly, their determination in environmental samples specially appears to be a challenging task for analytical chemists. In recent years, the development of analytical methods for the determination of rhodium has increased.

The aim of the present review is to evaluate the utility of atomic absorption spectrometry, applied for the quantification of rhodium in different materials, such as environmental, biological, metallurgical and geological samples.

Keywords: Rhodium determination; Atomic absorption spectrometry; Flame; Electrothermal atomization; Review

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Contents

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1. Introduction

Rhodium occurs naturally with other platinum metals only at very low concentration. Rhodium is mainly used with platinum in automobile catalysts and in catalysts in the chemical industry.

The determination of precious metals attracted the interest of analysts and developed rapidly because these metals are valuable and rare, yet also very important for many industrial processes and products. Their concentration levels are very low in many natural

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resources, metallurgical intermediates and environmental samples.

The low reactivity of the PGEs, towards single chemical reagents, their great chemical similarities, the formation of compounds of similar composition and properties, numerous oxidation states, the ability to form many species in a given oxidation state, their tendency to hydrolyse and also the formation of polynuclear complexes make determination, especially at low concentration levels, very difficult even for the experienced analyst.

Research has been carried out on developing reliable analytical methods for accurate determinations of traces of PGEs in different materials. Most of the attention has been focused on Pt determinations. A considerable volume of data has been accumulated on low-level Pt determinations at polluted sites and trends in concentrations of Pt over a period of years. However, corresponding Rh data are mostly missing. Analytical intercomparison projects have been performed in order to supply information on the applicability of different methods of Pt analysis; this is not yet the case for Rh.

The rhodium concentration in different materials can vary from $\mu g\, g^{-1}$ or lower to virtually 100%. Naturally, the wide range of sample types requires a variety of classical and instrumental methods or their combinations.

More often, the choice of the analytical technique depends on the availability and the level of occurrence of the metals and the nature of the sample matrix. For many years, atomic absorption spectrometry (AAS), both flame (FAAS) and electrothermal (ETAAS), has been widely used for the determination of PGEs in various materials. At present, AAS is the most widely used method for determination of rhodium as long as the sample can be dissolved in acids. Separation, preconcentration and dissolution of samples are the vital steps in many procedures, owing to the very low concentration of these metals in many samples and the complexity of the matrix. Among the AAS methods developed, the determinations for Pd and Rh are relatively sensitive. Efforts have been made to make methods reliable and practical. Hence, the precision, accuracy and reproducibility of these methods should be carefully checked.

This work is the continuation of other review, which summarise the determination of rhodium by spectrophotometric methods. The purpose of this review is to describe the analytical methods based on atomic absorption spectrometry techniques.

Atomic absorption involves a measurement of the reduction of intensity of optical electromagnetic radiation from a light source, following its passage through a cell containing gaseous atoms (the atom cell). Atomic absorption spectroscopy generally refers to the study of fundamental principles of this phenomenon, whereas atomic absorption spectrometry refers to its use for the quantitative determination of elements in samples, although these terms are often used interchangeably. AAS is applicable for the determination of most elements, almost all metals and metalloids and some non-metals, in a wide variety of samples, including biological, clinical, environmental, food and geological, and hence is one of the most commonly used techniques for elemental analysis. Two types of atom cells have been commonly used for AAS. The flame is widely because of its ease of use for elemental analysis at the part per million ($\mu g\, ml^{-1}$) levels. However, the use of a graphite furnace as the atomizer is used when a limited sample volume is available or lower analyte concentrations (part per billion, $ng\, ml^{-1}$ level) are present.

2. Flame atomic absorption spectrometry

2.1. Rhodium

In FAAS, the nebulised sample is introduced into either an air–acetylene or a nitrous oxide–acetylene flame. The absorption of the analyte atoms is compared against known standards. Due to less sensitivity of the technique and the low levels of analyte concentrations required, the FAAS technique generally finds use for Rh determinations in concentrates and Rh-rich samples.

Methods are suggested for increasing the sensitivity of the AA determination of rhodium by using a special nozzle on the burner which lengthens the effective thickness of the flame and by adding MeOH and $MgSO_4$ to the sample solution [1].

In other studies, very serious interferences were encountered with the air–C_2H_2 flame, while the N_2O–C_2H_2 flame was essentially free from such interferences, also other parameters were optimised [2,3]. The possible elimination of interferences is investigated by use of excess of Brilliant Green as a releasing agent, which has two roles: first, it forms a stable complex with the analyte, so that the Rh species will reach the flame independently; second, the excess of Brilliant Green scavenges the oxidizing species in the flame, providing favourable conditions for Rh atomisation [4]. More investigations about the interference problems and their possible solution were summarised in Table 1.

The analysis can be performed in organic solvents, which is a significant advantage of AAS compared to plasma methods. The solvent is facility removed, eliminating interferences. MIBK and ethanol were recommended as solvents and 1-heptanal as a buffering agent in organic solutions containing toluene, 1-hexene, 1-heptanol and 1-heptanal [5]. In addition to burner position, the composition of the organic solution significantly affected the absorbance. Ethanol has several advantages over MIBK as a solvent: it is cheaper, the smell is less unpleasant, the burner and chamber assembly keep cleaner and sensitivity is slightly better. Details of the use of the other organic solvents for rhodium analysis are described in some references, which appear in Table 1.

Industrial samples include catalyst, pure metals, sweep, scrap materials from the electronics industry and plating solutions. A significant portion of Rh is used as catalyst. The physical state in which the catalyst is used is often essential to arrive at a suitable sampling technique. In general, dried, crushed and ground material is used. The main goal of the first

Table 1
Determination of rhodium by FAAS

Sample matrix	Flame	Method	Reference
Aqueous solutions	Air–acetylene	Interference of Pd or Pt was minimised and the sensitivity was increased by using 1% U or La as spectral buffer	[13]
Synthetic mixtures	Air–acetylene	The interfering effects of different ions and organic compounds can be completely eliminated by adding excess *n*-butylamine	[14,15]
Aqueous solutions	Air–acetylene or nitrous oxide–acetylene	Interferences of acids and alkali salts and their elimination were investigated	[16]
Platinum concentrates	Air–acetylene	Addition of $ZnSO_4$ for eliminating interferences of Pt, $Na_2S_2O_7$ and Na_2SO_4	[17]
Aqueous and organic solutions	Air–acetylene	1–500 $\mu g\,ml^{-1}$ of Rh in C_6H_6–EtOH and cyclohexane-EtOH solutions by using ethylene glycol monomethyl ether as solvent. Optimum flame conditions and burner positions are discussed. The organic solvents have no significant effect in a lean fuel mixture, but burner position is critical	[18]
Aqueous and “cellosolve”-benzene solutions	Air–acetylene	This type of flame is used for increased sensitivity; the acetylene flow rate, and burner flame height are optimised for enhanced the linearity of response and maximum sensitivity	[19]
HAc, aqueous and MeOH media	Air–acetylene	DL of 0.2 $\mu g\,ml^{-1}$ in HAc medium	[20]
Hydroformulation products	Air–acetylene	Two methods were examined: (1) spectrophotometry with $SnCl_2$; relative error $\leq$5% for 0.02–8 wt.% Rh; analysis time 4.5 h and (2) AAS; 2.5–8% for 50–200 $\mu g\,ml^{-1}$ Rh; analysis time 20 min	[21]
Polymer-supported catalyst and organorhodium complexes	Air–acetylene	Addition of lanthanum nitrate (2%). Oxidative destruction of the organic material in a mixture of H_2SO_4 and H_2O_2	[22]
Organorhodium catalysts	Air–acetylene	Use of La as AAS buffer	[23]
High-purity iridium	Air–acetylene	Without prior separation; calibration curve is linear for 0.10–6.00 ng; detection limit is 0.03 ng	[24]
Solid and liquid polymer samples used in the rubber industry	Air–acetylene	A modified graphite furnace was used to volatilise the sample, after ashing, into the flame atomizer	[25]

stage of analysis, i.e. sample preparation and decomposition, is the quantitative and, if possible, rapid dissolution of the sample. This step determines largely the quality of the result and the duration of the complete analytical scheme. Fusing the samples in small crucibles, unlike the fusion process in the traditional fire assay technique, provides soluble salts of the sample materials. Mostly used for geological materials, the choice of fusion agent depends on the sample matrix. The advantages of fusion are easy and efficient attack of difficult matrices while the limitations are small sample weights, large concentration of sodium salts in the sample solutions and the introduction of contaminants from fusion reagents and crucible material [6,7].

Acid dissolution procedures are extensively used. Mixtures of different acids and also H_2O_2 are used in either open or closed vessels. Digestion on hot plates or by the microwave technique is popular. Additional separation and preconcentration steps are needed prior to the determination of the analyte. Often, acid extractions do not result in complete extraction of the rhodium especially for geological materials. Some of the reasons for this are particle size, varying sample matrix and incomplete wetting as well as the different experimental conditions used. The multi-acid digestion procedures offer advantages, such as low cost, low blanks and easy adaptability for batch analysis [8].

The use of AAS and UV–vis methods for the determination of rhodium in silica-supported catalysts is critically analysed to establish limits and fields of applicability to real working materials. The effectiveness of different digestion procedures of the metal phase is also widely studied as a function of the thermal treatment of the catalyst and the chemistry nature of the rhodium phase [9].

Preconcentration procedures are often necessary prior to the determination of rhodium. In these procedures, the analyte are concentrated from dilute solutions and are separated from major matrix elements and from minor amounts of other elements, which would interfere with their subsequent analysis. Solvent extraction, co-precipitation on Te, ion exchange separation are the most commonly used preconcentration methods.

Co-precipitation of Rh on a carrier, such as tellurium or selenium has been employed in many analytical procedures. The technique is more important for geological samples. In the routine procedure, a dilute salt solution of the carrier is added to the Rh solution. The tellurium or selenium is reduced to the metallic state by the addition of stannous chloride. The Te/Se precipitate, which collects the rhodium, is separated and processed [10].

Rh in solutions can be separated and concentrated from other elements by means of liquid–liquid extractions. Rhodium is determined in Cu, Ni, converter matte and anodic baths by extraction, with alkylaniline hydrochloride in MePh in the presence of Cl^- [11]. In addition, a new method for the quantitative extraction and separation of trace amounts of rhodium from nitric acid and sodium trichloroacetate media has been established based on the formation of an ion-association complex of hexahydrated rhodium cation and the trichloroacetate anion in tri-*n*-butyl phosphate. The effect of various factors on the extraction and back-extraction of rhodium has been investigated. The procedure was applied to determine rhodium traces in chloroplatinic acid and palladium chloride [12].

2.2. *Rhodium and other elements*

In the bibliography are collected numerous investigations in which the objective is to determine rhodium and other noble metals, principally PGEs. Their quantification is essential for an exploration programme to succeed, for effective monitoring of pollution levels or for evaluating the value of a spent catalyst. Considering that the concentration of these metals is typically very low (except in cases like alloys), analytical strategies need to include suitable sampling, effective solution preparation, preconcentration and analysis. The flame version (air–acetylene or nitrous oxide–acetylene) of the AAS has found few applications in the precious metal determinations. The reason lies in the poor sensitivity of the technique, interferences encountered and the level of analyte concentrations sought.

The parasitic absorption arising from high concentrations of the sample matrix during AA determinations of PGEs in chloroplatinic, chlororhodic and chloroiridic acids was measured by replacing the hollow cathode lamp with a continuous spectrum lamp to permit absorbance measurements at various wavelengths [26]. The dependence of the parasitic absorption on the gas flow rate to the flame, the matrix concentration and the wavelength is investigated; corrections for parasitic absorption were made for determinations of $\mu g\,ml^{-1}$ concentrations of Rh, Pt, Pd and Ir. In this way, to overcome specific and non-specific interferences a variety of releasing agents and buffers have been proposed, and separations, particularly from PGEs, are widely used to reduce interference problems.

The main goal of the first stage of analysis, i.e. sample preparation/decomposition, is the quantitative and, if possible, rapid dissolution of the sample. This step determines to great extent the quality of the result and the duration of the complete analytical scheme. Special precautions for the purification of reagents, especially fluxes, acids and vessels, are required in order to reduce the blank values. The techniques used for this purpose were fire assay, dry chlorination, acid dissolution and fusion. PGEs in solutions can be separated and concentrated from other elements by means of liquid–liquid extraction. The physical properties of octylaniline solutions in PhMe and polyalkylbenzene fraction, of tetraoctylammonium bromide in dichloroethane and of 1 M HCl were studied, and the effect of these solvents on the sensitivity of the AAS of PGEs is determined [27,28]. The increased sensitivity of determination of Rh, Pt, Pd, Ir and Ru during the atomisation of their organic solutions resulted from the decrease of the aerosol drop dimensions, increase of their introduction effectiveness, and increase of the flame temperature. In the same way, the extraction of noble metals with *p*-octylaniline at varying concentrations of different mineral acids is studied and optimum conditions were established for their separation from the base metals commonly present in Pt-bearing materials [29]. The noble metals, with the exception of Au, can be back-extracted with $HClO_4$ and determined by AAS. The procedure was successfully applied to analysis of mattes, sludge and flotation concentrates.

Because of the complex nature of the solution chemistry of the rhodium and the others PGEs and difficulties in developing reliable separation methods, especially for samples containing several PGEs, there is a focus on the wider application of various sorbents and complexes for the effective separation and preconcentration of these metals. The pairs Rh(III)–Pt(IV) and Ir(III)–Pt(IV) were separated as chloride complexes by liquid chromatography on Varion AT 400 and 660 anion exchangers. After separation, the metals were determined by FAAS [30]. A review by Al-bazi and Chow [31] details separation methods of the PGEs based on ion exchange chromatography and solvent extraction developed during 1950–1983.

Extraction of PGEs anionic chloride complexes was shown to be a very convenient method for the recovery of these metals from solutions of complicated composition. Amines and quaternary ammonium reagents are well known as highly efficient and selective extractants for PGEs. The extraction of metals from hydrochloric acid solutions is due to formation of ionic associates of PGEs chloride complexes with protonated amines. It was demonstrated that the extraction efficiency increases from mono- to polyamines.

Chemically modified silica and polymeric sorbents containing polyamino groups have been successfully utilised for the sorption preconcentration of PGEs in column mode.

Of all preconcentration and separation procedures, sorption possesses several advantages: large preconcentration factors that can be obtained in a short time, simplicity of phase separation and suitability for automation. Column based sorption techniques are frequently applied for the separation and preconcentration in flow injection atomic spectroscopy, first of all with AAS. A number of methods for separation and preconcentration of PGEs have been developed, i.e. sorption on metal hydroxides, chemically modified silica, and also on many types of polymeric sorbents. However, variety and "kinetic inertness" of PGEs coordination compounds (very slow ligand exchange rate) present essential difficulties in the determination of these metals.

The recovery of PGEs takes place rather slowly and often non-quantitatively. To accelerate sorption and increase the recovery, especially of rhodium, long heating of sample solution with the sorbent is normally required. Desorption of PGEs is also slow and often incomplete; eluents can destroy the sorbent. For this reason, there are only few examples of on-line flow injection sorption preconcentration of PGEs.

Solid phase extraction combines the benefits of solvent extraction and solid phase preconcentration, eliminating some of their drawbacks. It consists of the recovery of hydrophobic metal species on solid support of hydrophobic functionality. Desorption of metals is simply achieved by the change in solvent polarity. It does not require the use of concentrated acids or other aggressive reagents, and provides the opportunities of on-line combination of preconcentration and determination steps.

Some solid phase extraction systems proposed earlier for the on-line preconcentration of PGEs are characterised by low selectivity. Successful determination of PGEs with these techniques was demonstrated only for model laboratory solutions.

The development of a new selective system for on-line solid phase extraction of Rh, Pt and Pd and the design of an FIA–FAAS system have been proposed for the determination of these elements in solutions obtained by the decomposition of geological and technological samples [32].

For the determination of trace amounts of noble metals, in sulphate media by AAS, the metals were separated from the sulphate matrix by collection on NiS followed by fire assay, by precipitation as sulphides with thioacetamide, by ion exchange on phenylazodiaminopyridine resin, and by conversion of the sulphate to free H_2SO_4 by cation exchange chromatography followed by removal of the acid by evaporation [33]. The fire assay method gave low and inconsistent results.

The technique of fire assay (FA), known since medieval times, is still important for the determination of noble metals in geological and related materials. The method involves fusing a sample and flux mixture at approximately 1000 °C. The resultant melt separates into two immiscible phases. The upper glassy slag, which contains the alumino-silicates and base metals, is discarded. The denser phase, usually composed of either of the two collectors, i.e. leads in Pb-FA or nickel sulphide in NiS-FA, sinks to the bottom. The metals are strongly partitioned into this collector phase from which they may be subsequently separated for analysis [34,35]. A rapid, modified fire-assay technique is described for the determination of the total content of Rh, Pt, Pd and Au in ores and concentrates. The analytes can be determined individually by AA after cupellation of the Pb button at a low temperature [36].

The AA determination of Rh, Pt, Pd, Ru, Ir, Os, Au and Ag is reviewed by Sen Gupta [37], including sample treatment, methods for overcoming matrix effects, and operating parameters.

The adiabatic temperature and the efficiency of atomisation of 54 elements, including rhodium, in a methyl acetylene–nitric oxide flame were determined; optimum compositions of the flame were determined for each element and a comparison was made with the analytical characteristics of an acetylene–nitric oxide flame [38].

Table 2 describes the details of selected studies of rhodium and other metal ions.

3. Electrothermal atomic absorption spectrometry

GFAAS is a well-established technique with excellent sensitivity, and the equipments are available in many research laboratories.

In the GFAAS technique, a small volume of the sample is heated in a graphite tube and the absorption of the produced atoms is measured against standards. The residence time of individual atoms in the optical path is approximately 1–2 s as against 10^{-4} s for the flame version. The determination limits are thus lowered by at least one to two orders of magnitude depending on the element and sample volume.

The major disadvantages, however, are its inherently lower productivity and more severe interferences. Matrix modification, background correction, standard addition, etc., are useful in overcoming some of the interferences.

In the literature, there are few papers that describe the determination of only rhodium by GFAAS. For example, initially, Rh was determined in automotive catalyst by AAS using a flameless (heated graphite) furnace [84], in silver with chemical sample preparation directly in a graphite furnace [85].

The influence of some metal ions on the Rh signal is not simple and hence a separation step, prior to its determination, is necessary. The cellulose anion exchanger Cellex T was effective for separating Rh for platinum group and other heavy metals, and the method was applied to pyrite ore [86].

Relatively little information has so far been reported on the determination of trace rhodium in biological materials. ETAAS with a tungsten tube atomiser has been investigated under optimum conditions, the standard addition method was

Table 2
Determination of rhodium and other elements by FAAS

Elements	Sample matrix	Flame	Methods	Reference
Pd	Aqueous solution	Air–acetylene	Extraction with $CHCl_3$; 1-phenyltetrazoline-5-thione as a reagent for group preconcentration of the PGEs and Au	[39]
Pt	Cobalt oxide catalyst	Air–acetylene	Reduction of samples in a stream of H_2 and dissolved in aqua regia	[40]
Ru	Single crystal of cluster compounds: decomposition by H_2O_2 or autoclave methods	Air–acetylene	Buffering with $La_2(SO_4)_3$ or $KHSO_4$ to eliminate interferences	[41]
Pt, Pd	In the presence of copper sulphate and acetic acid	Air–acetylene	By ion exchange chromatography	[42]
Pt, Pd	Used and fresh alumina-supported and sieve catalysts	Air–acetylene	With La solution to eliminate chemical matrix interferences	[43]
Pt, Pd	Complicated samples	Air–acetylene	FI on-line separation-preconcentrtion with VS-II type anion exchange	[44]
Pt, Ru	Aqueous solutions	Nitrous oxide–acetylene	$La_2(SO_4)_3$ buffer for eliminating interferences	[45]
Ru; Ir	Solutions of complex composition	Air–acetylene	Examination of buffer properties of Na, Cd, Cu, La (sulphates)	[46]
Ru, Ir	Industrial sulphate solutions	Air–acetylene	Two variants of extraction using octylaniline hydrochloride	[47]
Pd, Au, Ag	Sludge, wastes and sands	Air–acetylene	Without spectral buffer; decomposition of samples by oxidative fusion with Na_2O_2 and leaching the flux cake with 2 M HCl	[48]
Pt, Pd, Au	In the presence of one or all of the other noble metals	Air–acetylene	Grid of the burner was improved; electronic voltage regulator was used to stabilize both the hollow cathode lamp and the spectrophotometer	[49]
Pt, Pd, Au	Ores after extraction from the base metals	Propane–butane–air	Simultaneously on a direct reading AAS, by using the non-absorbing Pt line at 304.2 nm	[50]
Pt, Pd, Au	In a silver collector	Air–C_2H_2 flame for Pt; air–C_3H_8 for Au, Pd, Rh	Sensitivities were: Pt, 150; Pd, 5; Rh, 2.5; Au, 5 $\mu g\,g^{-1}$ sample	[51]
Pt, Pd, Au	In small lead balls	Air–acetylene	Incomplete cupellation; La as spectral buffer	[52]
Pt, Pd, Au, Ag	In non-ferrous alloys and in metallic collectors	Air–acetylene	In pure solutions and also in the presence of large amounts of Cu, Pb, Zn and H_2SO_4, HCl and HNO_3	[53]
Pt, Pd, Au, Ag	Rocks	Air–acetylene	Sample was dissolved in aqua regia, SiO_2 removed with HF, coprecipitation by Te and $SnCl_2$ in HCl	[54]
Pt, Pd, Au, Ag	Geological materials	Air–acetylene	In Pb buttons from cupellation and extraction preconcentration with di(*o*-tolyl)thiourea by BuOAc	[55]
Pt, Pd, Au, Ag	Rocks and minerals	Air–acetylene	Aqua regia sample decomposition followed by Te coprecipitation	[56]
Pt, Pd, Ir	In the presence of a 20-fold excess of all other Pt metals	Air–acetylene	By addition of Na, Cu (sulphates) as spectroscopic buffer for eliminating interelemental interferences; in the ppm range	[57]
Pt, Pd, Ir	Hexachloroplatinic, iridic and rhodic acids	Air–acetylene	Li, Na or Cu (sulphates) as spectroscopic buffers to overcome matrix effects	[58]
Pt, Pd, Ir	Alloys and tailings of metallurgical production	Air–acetylene	Ag and Au were separated by extraction with tert-dodecylmercaptan and Et_2O, respectively	[59]
Pt, Pd, Ir	These elements in the presence of each other	Air–acetylene	Sorption and solvent extraction were used for preconcentration	[60]

Table 2 (*Continued*)

Elements	Sample matrix	Flame	Methods	Reference
Pt, Pd, Ir	Slag, graphitised materials, ashes, dusts from electrostatic precipitators and other lean metallurgical samples	Air–acetylene	Extraction into $CHCl_3$ with 1,1-hexamethylene-3-phenylthiourea	[61]
Pt, Pd, Ir	Rh in high purity Pt with a correction for non-specific absorbance of the Pt matrix	Air–acetylene	Optimum conditions for the simultaneous determination without any initial separation	[62]
Pt, Pd, Ir, Au	A wide range of platiniferous materials	Air–acetylene	Initial extraction of Au, a simultaneous extraction of Pt and Pd as iodides, and a subsequent simultaneous extraction and preconcentration of Rh and Ir as their 2-mercaptobenzothiazole complexes in MIBK	[63]
Pt, Pd, Ir, Au	Various noble metal solutions and a solid platiniferous sample	Air–acetylene	Isolation of Ir after simultaneous extraction of Rh, Pt, Pd and Au as their 2-mercaptobenzothiazole-$SnCl_2$ complexes into $CHCl_3$	[64]
Pt, Pd, Ir, Au, Ag	Aqueous solutions	Air–acetylene	Study of interference effect caused by aluminium	[65]
Pt, Pd, Ru, Ir	Products of the processing of copper–nickel slimes	Air–acetylene	–	[66]
Pt, Pd, Ru, Au	In the presence of base metals	Air–acetylene	V in $HClO_4$ medium is used as a releasing agent for the removal of interferences	[67,68]
Pt, Pd, Ru, Au	Cu-ore and Ni-ore concentrates and synthetic mixtures	Air–acetylene	After precipitation concentration on copper sulphide	[69]
Pt, Pd, Ru, Ir, Au	Matte-leach residues	Air–acetylene	Fusion with Na_2O_2 in a Zr crucible at a dull-red heat; the residue was leached with an acid	[70]
Pt, Pd, Ru, Ir, Au	Ore concentrates	Air–acetylene	By extraction from 2 to 3 M HCl into 0.5–1 M $C_{8–10}$ alkylanilines in MePh	[71]
Pt, Pd, Ru, Ir, Au	Natural and industrial samples	Air–acetylene	Flame and graphite furnace after preconcentration by lead involving incomplete cupellation	[72,73]
Pt, Pd, Ru, Ir, Au, Ag	Aqueous solutions	Air–acetylene	Optimising the measuring conditions, such as C_2H_2 and air flow rates, burner position, etc.	[74]
Pt, Pd, Ru, Ir, Au, Ag	Natural materials	Air–acetylene	Two types of pulse atomizers are suggested: microsound-flame-adaptor and graphite red in air	[75]
Pt, Pd, Ru, Ir, Os	Aqueous solutions	Air–acetylene	Comparison with the use of a tube-type C rod atomizer	[76]
Pt, Pd, Ru, Ir, Os	Aqueous solutions	Toluene–nitrous oxide	Study of properties and the possibility of the use of this flame	[77]
Pt, Pd, Ru, Ir, Os	Products of Ni and Cu slime processing	Air–acetylene	By using preconcentration by coprecipitation on a mixed collector (Cu sulphide-2-mercaptobenzothiazole)	[78]
Pt, Pd, Ru, Ir, Os, Au, Ag	Ores, rocks, and tailings	Air–acetylene	By injecting microvolumes of solutions from preconcentration into flame or flame-adapter atomisers	[79]
Pt, Pd, Ru, Ir, Os, Au, others	Native silver	Air–acetylene	By separating the Ag as AgCl by double precipitation	[80]
Various elements	Various materials	Air–acetylene	Design characteristics, sensitivity and various analytical factors using a microprobe-flame-adapter atomiser	[81]
Many elements	High-purity silver	Air–acetylene	After extractive separation of the matrix; $CuSO_4$ as buffer for elimination of interferences	[82]
Many elements	Highly purified gold	Air–acetylene	After matrix separation by extraction in $CHCl_3$	[83]

adapted for the determination of rhodium in biological samples, the recovery of spiked-rhodium was in the range of 97.4–107% [87]. In the similar way, a new concentration method using Mg–W cell-electrodeposition has been developed; the method was combined with ETAAS with a tungsten atomiser. Under optimal conditions, the detection limit was 13 ng ml^{-1}. The method was applied for the determination of Rh in river and seawater; the recovery of rhodium spiked environmental samples was in the range of 95.6–109% [88]. An automatic on-line FI-GFAAS method for the determination of trace amounts of Rh was used employing a chelating resin microcolumn [1,5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide (PSTH)] immobilised on an anion-exchange resin (Dowex 1x8-200) placed in the autosampler arm, for the separation and preconcentration from environmental samples; the detection limit is 0.3 ng ml^{-1} [89].

Research has been carried out on developing reliable analytical methods for accurate determination of rhodium and other noble metals; recent interest in the medical and industrial significance of these metals has been accompanied by an increasing interest in their determination at low levels. Thus, the use of AA with a HGA-72 graphite furnace for the determination of Rh, Pt, Pd and Au allows the decrease of their detection limits by two orders compared with results obtained by a flame atomizer. It also decreases the number and size of the samples needed for analysis; the method can be used to analyse this metals in silver alloys [90].

The pyrolytic treatment of graphite tubes were investigated [91]. Enhancement factors of 1.9–3.4 were obtained and sensitivities for Pt, Pd, Rh, Ru and Ir were 97, 23, 11.5, 27 and 170 pg for 1% absorption, respectively. These sensitivities were achieved at lower atomisation temperatures and the lifetime of the graphite tubes was extended.

The main goal of the fist stage of analysis, i.e. sample preparation/decomposition, is the quantitative and, if possible, rapid dissolution of the sample. This step determines largely the quality of the result and the duration of the complete analytical scheme. Special precautions for the purification of reagents, especially fluxes, acids and vessels, are required in order to reduce the blank values.

Trace quantities of the same metals were separated and concentrated by fusion; nickel sulphide was used as the collector, and the analyte were measured in the resulting acid solution. The method, which is described in detail, is applicable to the determination of these elements in ores, tailings, and geological materials [92]. After pressure digestion at 170 °C of rock samples with HF and aqua regia, the noble metals Rh, Pt, Pd, Ir and Au are separated from the matrix with selective adsorption on Sarafion NMRR ion-exchange resin. The metals are then determined in the thiourea eluate [93]. The reliability of the procedure was confirmed by analysis of rock standards and meteoric material. In other study, traces of the same elements were determined in natural and synthetic samples by GFAAS after preconcentration on chelating sorbents [94]. Polyorgs IV and Polyorgs XIN were used for preconcentration from aqueous and organic solutions, respectively. Advantages of direct introduction of sorbent suspensions into graphite furnace include faster analysis, elimination of possible contamination during sample preparation, elimination of the loss of analytes associated with the formation of volatile carbonyl chlorides during wet decomposition of polymeric matrices, and enhancement of the analytical signal in comparison to the use of chloride solutions. In addition, microwave heating improved the rate of Pd^{2+} and Rh^{3+} sorption by Polyorgs IV from 1 M HCl [95]. Rapid sample preparation for the atomic absorption finish involved introduction of concentrate suspensions stabilised by glycerol or polyethylenglycol into the furnace. In other study, a microwave digestion procedure was evaluated for the determination of the Pt, Pd and Rh in small amounts of animal tissue [96]. Due to the lack of certified biological standard reference materials for this metals, were performed inter-laboratory comparison using adsorptive cathodic stripping voltammetry after digestion of the samples by high-pressure ashing for the determination of Pt and Rh and total-reflection X-ray fluorescence analysis after co-precipitation of Pd with mercury for the determination of Pd, as reference methods. The combination of microwave digestion and GFAAS is a very rapid and relatively cheap method for routine PGEs analysis in large numbers of animal tissue samples with PGEs concentrations exceeding the upper ng g^{-1} range as occur in experimental studies or in the medical sector after treatment with Pt-anti-cancer drugs.

The main advantage of preconcentration procedures is the possibility of determining lower analyte concentrations and avoiding matrix effects by effective separation of the analyte from interfering matrix components. In this respect flow systems, combined with liquid–liquid extraction, ion exchange, sorbent extraction and electrochemical deposition are of growing interest; a flow system combined with a segmentation technique was used to develop an efficient on-line sorbent extraction preconcentartion system for palladium, platinum and rhodium [97]. The investigated metals were preconcentrated as their bis(carboxylmethyl)dithiocarbamate (CMDTC) chelates on a microcolumn packed with XAD-4 after the off-line addition of solid CMDTC of the sample solution containing $SnCl_2$ and HCl.

Two methods for determining trace and ultratrace amounts of noble metals, except Os, in ores, concentrates, mattes and silicate and iron-formation rocks are applied [98]. After sample decomposition with HF and aqua regia, followed by fusion of any insoluble residue with Na_2O_2, the noble metals are separated from the matrix elements by either cation exchange or coprecipitation with tellurium. The resulting eluate, or the solution obtained after dissolution of the tellurium precipitation, is evaporated to dryness and the metals are ultimately determined in a 1 M HCl medium. The ion-exchange method is recommended for the determination of μg g^{-1} levels of Au, Ag and PGEs, whilst the Te co-precipitation method is recommended for ng g^{-1} levels of PGEs. Results obtained by these methods for 15 international reference samples are compared with other published data.

Table 3
Determination of rhodium and other elements by GFAAS

Elements	Sample matrix	Methods	Reference
Pt	γ-Alumina catalysts	By glow discharge atomisation	[109]
Pt	Aqueous solutions	Solvent extraction with *N*,*N*-di-*n*-hexyl-*N*′-benzoylthiourea/toluene accelerated by the presence of tin(II) chloride	[110]
Pt	Metallurgical	As 2-mercaptobenzothiazole complexes by means of molten naphthalene extraction	[111]
Pt	Geological	After their separation and enrichment with VS-II type anion exchange fibber	[112]
Pt, Pd	Silver alloy	Using a graphite boat and an electrothermal atomizer	[113]
Pt, Pd	Silver and its alloys	Develop of a program for automated direct determination	[114]
Pt, Pd	18 U.S. geological survey reference materials	Preconcentration by the classical Pb-fire assay	[115]
Pt, Pd	Aqueous solutions	Nickel sulphide fire assay	[116]
Pt, Pd	Ores of CuS–NiS	Preconcentration with the Polyorgs-XXVII sorbent	[117]
Pt, Pd	Ceramic-supported catalyst	Analytical parameters were optimised for this type of samples; to simplify the sample preparation procedure and to prevent the possible losses of elements, the treatment of the previously ground sample with a mixture of mineral acids is recommended	[118]
Ru, Ir	High-purity platinum	Extraction with isoamyl alcohol–isobutyl methyl ketone mixture	[119]
Pt, Pd, Au	Silicates roks	Extraction and enrichment by coprecipitation with selenium and tellurium	[120]
Pt, Pd, Au	Mn crust, natural water, geological and biological standards	Upon extraction with Se via a coprecipitation technique, elaborated as a microtechnique	[121]
Pt, Pd, Ir	Cu–Ni ores, chromite ore, molybdenite ore	Sorption preconcentration as chlorides on the chelating sorbent PVB-MP-20T and analysis of suspensions of sorbents	[122]
Pt, Pd, Ir	Silicate rocks	Concentration into a Pb button and cupellation	[123]
Pt, Pd, Ru	Road dust	Complete microwave-assisted acid digestion of the sample with HNO_3-HF-$HClO_3$/$HClO_4$ mixtures in a high-pressure Teflon bomb; metals deposited on the inner wall of a graphite tube in a flow through cell of 1 ml volume; using a three-electrode arrangement for the electrodeposition	[124]
Pt, Pd, Ru	Environmental samples	By GFAAS and inductively coupled plasma-optical emission spectrometry	[125]
Pt, Pd, Ru, Ir	In sulphate solutions	Typical drying, ashing and atomisation were 150, 1000–1400 and 2400–2650 °C	[126]
Pt, Pd, Ru, Ir	Pt ore reference material	Determination of optimum conditions measurements and mutual interference limits	[127]
Pt, Pd, Ru, Ir	PGEs dopants in silicon	Sensitivities ($\times 10^{-11}$ g, 1% absorption): 28, 18, 5.8, 2.8, and 2.6 for Ir, Pt, Ru, Rh and Pd, respectively	[128]
Pt, Pd, Ru, Ir	Geological materials	D001-ML macroporous resin used to separate metals as chloro complexes from base metal ions in HCl medium	[129]

Table 3 (*Continued*)

Elements	Sample matrix	Methods	Reference
Pt, Pd, Ru, Ir, Au	Ore and enriched tail	Fire-assay and extraction with toluene containing alkylaniline hydrochloride and petroleum sulphide	[130]
Pt, Pd, Ru, Ir, Os	Aqueous solutions	With pyrolytic coating; detection limit ($\times 10^{-11}$, g): Os 50, Ir 10, Pt 5, Ru 3, Pd and Rh 1	[131]
Pt, Pd, Ru, Ir, Os	Acid solutions	In concentrations 10^{-3} to 10^{-7} M were determined by extraction with bis(2-ethylhexyl) dithiophosphate from HCl, H_2SO_4or H_3PO_4 solutions of their mixtures	[132]
Pt, Pd, Ru, Ir, Os	Technological solutions and solid products	After sorption preconcentration on a thioether polymer	[133]
Pt, Pd, Ru, Ir, Os	10 Reference materials	Effects of fusion charge composition using collection into a minimised nickel sulphide button	[134]
Pt, Pd, Ru, Ir, Os	Slurries of concentrates	Microwave dissolution of samples followed by dynamic sorption preconcentration of the PGEs on a polystyrene based sorbent containing diethylenetriamine groups	[135]
Pt, Pd, Ru, Ir, Os	Geological and environmental (soil, sludge, street-sweeping) samples	With a variant of nickel sulphide fire assay	[136]
Pt, Pd, Ru, Ir, Os	Environmental samples	High-speed self reversal with electrothermal atomisation in a graphite tube furnace	[137]
Pt, Pd, Ru, Ir, Os, Au	Cu base standards	Sorption on polyorgs XI-H (polyacrylonitrile fibbers loaded with a chelating sorbent containing heterocyclic amino groups); the sorbent was dried and its suspension in DMF or DMSO was analysed	[138]
Pt, Pd, Ru, Ir, Os, Au	Copper–nickel sulphide ores	Autoclave decomposition of sample; collective extractive preconcentration of metals with a mixture of alkylaniline hydrochloride and petroleum sulphides	[139]
Pt, Pd, Ru, Ir, Au, Ag	Aqueous solutions	By carbon furnace; for 20 μl sample volume, sensitivities ($\times 10^{-3}$, in $\mu g\,ml^{-1}$) with 1% absorption were: Ir 38, Pt 23, Ru 19, Rh 5.8, Pd 4.5, Au 0.89 and Ag 0.21	[140]
Pt, Pd, Ru, Ir, Au, Ag	Silicate rocks, ores and metallurgical samples	Attacking of the samples with HF and aqua regia, preconcentration by ion-exchange chromatography and measuring in a simultaneous multi-element GFAAS with Zeeman background correction	[141]
Pt, Pd, Ru, Ir, Os, Au, Ag	Aqueous solutions	Using both common graphite tube and pyrolytic graphite tube: comparative study	[142]
Pt, Pd, Ru, Ir, Os, Au, Ag	Chromites and related materials	Use of a mixture of $KBrF_4$ and KHF_2 obtained in situ by adding liquid BrF_3 to a mixture of KHF_2 and sample powder	[143]
Pt, Pd, Ru, Ir, Os, Au, Ag	Refractory geological and process materials	Decomposition procedure based on the oxidizing fluorination of samples with subsequent sulphatisation	[144]
Pd, Au, Ag, Cu	Aqueous solutions	Preconcentration using a Mg–W cell-electrodeposition; with a tungsten atomiser	[145]

Table 3 (*Continued*)

Elements	Sample matrix	Methods	Reference
Ba, Cr, Fe, Mn, Mo, Pd, Sr	Nuclear high- and medium-activity waste solutions	Based on that analytical technique was devised and used for remote operation under safe conditions; the graphite furnace and the associated autosampler are enclosed in a specially devised glove box	[146]
19 Elements	High-purity gold	Solvent extraction into methyl ethyl ketone/chloroform	[147]
Various elements	Natural waters and technological samples	Analysis of concentrates on Polyorgs sorbents introduced into the furnace in the form of a suspension	[148]

A method for the separation of Au, Pd, Pt, Rh, Ag and some important pathfinder elements (Se and Te) from geological samples at trace levels is presented [99]. The elements are separated from the matrix after dissolution by reductive co-precipitation using mercury as a collector and tin(II) chloride as a reductant.

Optimum condition for the GFAAS of platinum-group metals have been reported previously [100,101]. Instrumental conditions for the determination of Pt, Pd and Rh are described for two instruments [102]. The effects of acid concentration on the signals of absorbance were found to be instrument dependent. This instrument dependence is discussed in terms of the geometries of the various tubes employed in the furnaces. A comparison is made of voltage control and temperature control facilities for the atomisation of the three metals. On the other hand, a curved mini-platform was designed, which is made of totally pyrolytic graphite [103], the effect of over 20 diverse elements on determination of Rh and Pt are investigated by using this technique. Also, new tantalum carbide coated platforms have been tested as atomisation surfaces [104]. The aim was to investigate the behaviour of these platforms towards common interferents, compared with those of standard pyrolytic graphite platforms; the analytes studied were Rh, Sn and Se, the interfering cations were Cr, Fe, Na, Mg, Zn and Al. In the last years, generally, the most robust commercially available GFAAS instruments offer the possibilities for stabilised temperature platform furnace (STPF) conditions and Zeeman-effect background correction in connection with a transversely heated graphite atomiser (THGA). GFAAS systems based on this concept provide higher and more homogeneous temperature conditions in the atom reservoir for the vaporization/atomisation of rhodium, and a less intensive extent of interferences; also, these conditions imply some two orders of magnitude linearity of the calibration.

As was aforementioned, the ultra-trace levels of PGEs in environmental samples requires pre-concentration of the analytes and/or separation of the matrix for their detection by GFAAS; in this way, a method for separation and determination of Rh, Pt and Au by HPLC coupled with GFAAS was developed [105]. The analytical conditions of reverse-phase ion-pair HPLC are discussed and an excellent separation of $RhCl_5^{2-}$, $PtCl_6^{2-}$, and $AuCl_4^-$ was obtained using tetrabutylammonium bromide as ion-pair reagent in methanol–H_2O system. Also, in order to develop a simple analytical procedure for determining the content of Pd, Pt and Rh in samples of stream and lake sediment, the ability of a molecular recognition ligand (Superlig 202) to extraction quantitative these three elements from solutions loaded with different ions was assessed [106].

The majority of samples are solids, which are generally converted to solutions, and introduced in that form into the graphite tube; however, the direct analysis of solids is also possible, and two basic techniques have been employed: slurry sampling, in which a powdered material is suspended in a solution that is aspirated into the atom cell, and solid sampling, in which a solid is directly inserted into the graphite furnace; for example, hybrid sample preparation involved treating the alloy with concentrated HCl on a graphite boat, drying, transfer of the boat into the graphite furnace, matrix removal by volatilisation of $PbCl_2$ at 800 °C, decomposition at 1000–1600 °C, and atomisation at 2600 °C [107]. The method was used for determining PGEs in Pb alloy buttons from fire assay of various materials (basalts, Cu–Ni sulphide ores). In relation with insoluble particles in the nuclear fuel cycle waste, the solid sampling GFAAS was used to determine Rh, Mo, Ru and Pd in such waste [108]; the samples must be handled in glove boxes or in hot cells with a robot by using the slurry technique.

The details of studies by various workers are furnished in Table 3.

4. Conclusions

PGEs, mainly released by vehicle exhaust catalyst, have been significantly accumulated in environmental matrices over the past decades. For this reason, investigations involving determinations of background and very low levels of rhodium for the purpose of exploration, biological evaluation and monitoring of environmental impact have led to the development of new analytical methods.

As can be seen, in AAS, both flame and electrothermal atomisation have been used extensively in many laboratories.

Improvements in sample treatments and preconcentration steps in order to enhance recoveries of the rhodium, and to reduce contamination from chemicals and equipment, have assisted in the achievement of better results. Much of the work has been carried out with an air–acetylene flame. To overcome specific and non-specific interferences, a variety of releasing agents and buffers have been proposed. Separations, particularly from PGEs, are widely used to reduce interference problems. Although this approach is more time consuming, it has the added advantage of effecting a preconcentration of rhodium.

In environmental samples, the low concentration of rhodium together with the high concentration of interfering matrix components often requires a pre-concentration/enrichment step combined with a matrix separation for their detection by AAS.

The last developments of the GFAAS, in general, but that also affect to the determination of rhodium, include the use of platform or probe atomisation to ensure atomisation occurs under isothermal conditions, integrated absorbance, pyrolytically coated graphite tubes, an autosampler, fast heating rates during the atomisation step, fast electronics, and modern methods of background correction; the ease of use and analytical performance of GFAAS were significantly improved by modern furnace technology. In the last years, fast furnace programs and multielemental GFAAS were major foci to increase the sample throughput of the technique. Because the GFAAS method is relatively inexpensive and easy to operate it has found wide application for rhodium determination including analysis of rocks, ores, alloys and waste solutions.

References

[1] V.L. Ginzburg, D.F. Makarov, I.G. Satarina, Zh. Anal. Khim. 24 (1969) 264.
[2] M.G. Atwell, J.Y. Hebert, Appl. Spectrosc. 23 (1969) 480.
[3] S. Kallmann, E.W. Hobart, Anal. Chim. Acta 51 (1970) 120.
[4] M.M. El-Defrawy, A. Abadía, M. El-Shamy, Asian J. Chem. 5 (1993) 1047.
[5] M. Kauppinen, K. Smolander, Anal. Chim. Acta 285 (1994) 45.
[6] D.E. Harrigton, W.R. Bramstedt, Atom. Absorp. Newslett. 15 (1976) 125.
[7] W.R. Bramstedt, D.E. Harrington, K.M. Andrews, Talanta 24 (1977) 665.
[8] I.A. Ryzhak, Z.I. Sukhareva, A.P. Zolotareva, B.M. Talalaev, Zav. Labor. 48 (1982) 35.
[9] S. Recchia, G. Zanderighi, A. Fontana, C. Dossi, Ann. Chim. 87 (1997) 359.
[10] M.M. Schnepfe, F.S. Grimaldi, Talanta 16 (1969) 1461.
[11] V.V. Vasil'eva, V.V. Androsova, Zh.O. Badmaeva, L.M. Gindin, E.N. Gil'bert, Seriya Khim. Nauk. 4 (1980) 121.
[12] K.Z. Hossain, T. Honjo, Fresen. J. Anal. Chem. 368 (2000) 480.
[13] W. Heinemann, D. Werk II, Fresen. Zh. Anal. Chem. 281 (1976) 291.
[14] M.A. Mostafa, M.A. Kabil, Indian J. Chem. 24A (1985) 260.
[15] M.A. Kabil, M.A. Mostafa, Rev. Roum. Chim. 30 (1985) 631.
[16] H. Watanabe, I. Tadani, K. Hiro, Hiroshima-kenritsu Seibu Kogyo Gijutsu Senta Hokoku 28 (1985) 44.
[17] A. Hofer, Fresen. Zh. Anal. Chem. 258 (1972) 285.
[18] J.R. Deily, Atom. Absorp. Newslett. 6 (1967) 65.
[19] K.J. Garska, Atom. Absorp. Newslett. 15 (1976) 38.
[20] R. Hebisch, G. Emrich, H. Dilcher, Zeitschrift fuer Chem. 29 (1989) 217.
[21] N.I. Pakhomova, A.V. Kashcheeva, V.I. Ostroushko, Neftepererabotka Neftekhimiya 4 (1988) 21.
[22] F.R. Hartley, S.G. Murray, P.N. Nicholson, J. Organomet. Chem. 231 (1982) 369.
[23] T.I. Belikova, Deposited Doc. (VINITI 6343-82) (1982) 143.
[24] T. Wang, H. Zhai, X. Fang, Y. Zhang, S. Li, Guangpuxue Guangpu Fenxi 7 (1987) 50.
[25] R. Kannipayoor, J.C. Van Loon, Spectrosc. Lett. 20 (1987) 871.
[26] G. Pannetier, P. Toffoli, Bull. Soc. Chim. Fr. 7 (1972) 2977.
[27] T.V. Lanbina, I.G. Yudelevich, V.A. Poluboyarov, Seriya Khim. Nauk. 5 (1974) 78.
[28] A.A. Vasilyeva, I.G. Yudelevich, L.M. Gindin, T.V. Lanbina, R.S. Shulman, I.L. Kotlarevsky, V.N. Andrievsky, Talanta 22 (1975) 745.
[29] C. Pohlandt, M. Hegetschweiler, Rep.-Nat. Inst. Metall. 1940 (1978) 19 pp.
[30] K. Brajter, K. Slonawska, Z. Vorbrodt, Chem. Anal. 24 (1979) 763.
[31] S.J. Al-Bazi, A. Chow, Talanta 31 (1984) 815.
[32] I.A. Kovalev, L.V. Bogacheva, G.I. Tsysin, A.A. Formanovsky, Y.A. Molotov, Talanta 52 (2000) 39.
[33] K. Dixon, D.J. Nicolas, R.V.D. Robert, E. Van Wyk, Rep.-Nat. Inst. Metall. 1739 (1975) 26 pp.
[34] R.V.D. Robert, E. Van Wyk, Rep.-Nat. Inst. Metall. 1705 (1975) 9 pp.
[35] G.E.M. Hall, J.C. Pelchat, Chem. Geol. 115 (1994) 61.
[36] E. Van Wyk, Rep.-Nat. Inst. Metall. 2068 (1980) 8 pp.
[37] J.G. Sen Gupta, Miner. Sci. Eng. 5 (1973) 207.
[38] A.A. Pupyshev, I.G. Evdokimova, J. Appl. Spectrosc. 65 (1998) 10.
[39] A.V. Radushev, G. Ackermann, Zh. Anal. Khim. 32 (1977) 1287.
[40] B. Rózanska, Analyst 120 (1995) 407.
[41] K. Smolander, I. Mustonen, J. Pursiainen, T. Saari, T. Venalainen, T.A. Pakkanen, Fresen. Zh. Anal. Chem. 329 (1987) 27.
[42] Y.M. Ham, Y.G. Lee, S.K. Yoo, J.H. Chung, J.C. Hyun, S.K. Lee, Y.J. Yoo, Yongu Pogo-Kungnip Kongop Sihomwon 37 (1987) 41.
[43] M. Merdivan, R.S. Aygun, N. Kulcu, Atom. Spectrosc. 18 (1997) 122.
[44] J. Qi, C. Bao, G. Jiang, M. Zou, H. Xu, N. Lu, X. Wang, Jilin Daxue Xuebao, Lixueban 40 (2002) 408.
[45] H. Urbain, M. Cattenot, Analusis 7 (1979) 196.
[46] D.F. Makarov, Y.N. Kukushkin, T.A. Eroshevich, Zh. Anal. Khim. 29 (1974) 2128.
[47] V.V. Belova, A.A. Vasil'eva, N.V. Androsova, Seriya Khim. Nauk. 1 (1983) 89.
[48] A.S. Khalonin, E.G. Novakovskaya, L.B. Kalinina, V.R. Brosse, Zav. Labor. 48 (1982) 35.
[49] A. Strasheim, G.J. Wessels, Appl. Spectrosc. 17 (1963) 65.
[50] P.B. Zeema, J.A. Brink, Analyst 93 (1968) 388.
[51] D.F. Makarov, Y.N. Kukushkin, T.A. Eroshevich, Z. Prikladnoi Khim. 47 (1974) 1215.
[52] L.P. Kolosova, N.V. Novatskaya, E.G. Vinnitskaya, Zav. Labor. 42 (1976) 508.
[53] V.L. Ginzburg, D.M. Livshits, G.I. Satarina, Zh. Anal. Khim. 19 (1964) 1089.
[54] B.J. Fryer, R. Kerrich, Atom. Absorp. Newlett. 17 (1978) 4.
[55] N.L. Fishkova, O.P. Talypina, Zh. Anal. Khim. 38 (1983) 452.
[56] G.P. sighinolfi, C. Gorgona, A.H. Mohamed, Geostandard Newslett. 8 (1984) 25.
[57] A. Janssen, F. Umland, Fresen. Zh. Anal. Chem. 251 (1970) 101.
[58] P. Toffoli, G. Pannetier, Int. Congr. Atom. Absorp. Atom. Fluoresc. Spectrom. 2 (1971) 707.
[59] E.A. Starseva, N.M. Popova, V.P. Khrapai, I.G. Yudelevich, Seriya Khim. Nauk. 2 (1978) 31.
[60] A.N. Savel'eva, N.P. Khairulina, Zh. Anal. Khim. 33 (1978) 1380.

[61] E.A. Startseva, N.M. Popova, V.P. Khrapai, I.G. Yudelevich, Seriya Khim. Nauk. 5 (1980) 94.
[62] K. Brajter, K. Slonowska, Z. Vorbrodt, Chem. Anal. 27 (1982) 239.
[63] A. Diamantatos, Anal. Chim. Acta 131 (1981) 53.
[64] A. Diamantatos, Anal. Chim. Acta 147 (1983) 219.
[65] Z. Liu, T. Lin, Guangpuxue Guangpu Fenxi 9 (1989) 50.
[66] O.A. Shiryaeva, L.N. Kolonina, G.I. Molofeeva, E.V. Marcheva, Zh. Metall. (1982), Abstract no. 11K62.
[67] R.C. Mallett, D.C.G. Pearton, E.J. Ring, Nat. Inst. Met. Repub. S. Afr. Rep. (1970) No. 1086 5 pp.
[68] T.W. Steele, R.C. Mallet, D.C.G. Pearton, E.J. Ring, Report (1970) NIM-1086, 11 pp.
[69] M.L. Rakhlina, M.Y. Lomteva, G.I. Ermolina, Zav. Labor. 51 (1985) 91.
[70] G. Wall, J. Royal, K. Dixon, R.C. Mallett, Rep.-Nat. Inst. Met. 1837 (1976) 12 pp.
[71] E.N. Gil'bert, N.V. Korneva, Z.O. Badmaeva, I.G. Yudelevich, Zav. Labor. 45 (1979) 714.
[72] L.P. Kolosova, N.V. Novatskaya, R.I. Ryzhova, A.E. Aladyshkina, Zh. Anal. Khim. 39 (1984) 1475.
[73] L.P. Kolosova, A.E. Aladyshkina, N.V. Novatskaya, R.I. Ryzhova, J. Anal. Chem. USSR 39 (1984) 1173.
[74] W. Heinemann, D. Werk II, Fresen. Zh. Anal. Chem. 280 (1976) 127.
[75] E.D. Prudnikov, L.P. Kolosova, V.K. Kalachev, Y.S. Shapkina, N.V. Novatskaya, Y.A. Bychkov, Zh. Anal. Khim. 33 (1978) 468.
[76] G.L. Everett, Analyst 101 (1976) 348.
[77] G.P. Gracheva, V.N. Morozov, L.K. Popyalkovskaya, Y.D. Skudaev, Zh. Prikl. Spektrosk. 31 (1979) 211.
[78] L.N. Kolonina, O.A. Shiryaeva, G.I. Malofeeva, E.V. Marcheva, Zh. Anal. Khim. 35 (1980) 92.
[79] E.D. Prudnikov, Y.S. Shapkina, Zh. Anal. Khim. 38 (1983) 2019.
[80] J.G. Sen Gupta, Anal. Chim. Acta 63 (1973) 19.
[81] E.D. Prudnikov, Zh. Anal. Khim. 30 (1975) 232.
[82] E.A. Startseva, N.M. Popota, I.G. Yudelevich, N.G. Vanifatova, Y.A. Molotov, Fresen. Zh. Anal. Chem. 300 (1980) 28.
[83] E.A. Startseva, N.M. Popota, I.G. Yudelevich, Seriya Khim. Nauk. 4 (1980) 127.
[84] N.M. Poter, Anal. Chem. 50 (1978) 769.
[85] N.K. Bel'skii, L.A. Nebol'sina, L.K. Shubochkin, G.N. Verkhoturov, Zh. Anal. Khim. 35 (1980) 799.
[86] K. Slonawska, K. Brajter, J. Anal. Atom. Spectrom. 4 (1989) 653.
[87] K. Ohta, J. Ogawa, T. Mizuno, Anal. Lett. 30 (1997) 787.
[88] S. Kaneco, J. Ogawa, K. Ohta, S. Itoh, T. Mizuno, Talanta 46 (1998) 139.
[89] F. Sánchez Rojas, C. Bosch Ojeda, J.M. Cano Pavón, Talanta 64 (2004) 230.
[90] N.K. Bel'skii, L.A. Nebol'sina, M.I. Yuz'ko, T.A. Fomina, E.F. Shubochkina, L.K. Shubochkin, Zh. Anal. Khim. 33 (1978) 336.
[91] Y. Gao, Z. Ni, Xiyou Jinshu 1 (1982) 99.
[92] J. Haines, R.V.D. Robert, Gov. Rep. Announc. Index (U.S.) 82 (1982) 5217.
[93] K. Kritsotakis, H.J. Tobschall, Fresen. Z. Anal. Chem. 320 (1985) 15.
[94] I.V. Kubrakova, G.M. Varshal, T.F. Kudinova, Zh. Anal. Khim. 42 (1987) 126.
[95] I.V. Kubrakova, M. Abuzveida, T.F. Kudinova, T.P. Shemarykina, N.M. Kuz'min, Zh. Anal. Khim. 44 (1989) 1793.
[96] S. Zimmermann, J. Messerschmidt, A. Bohlen, B. Sures, Anal. Chim. Acta 498 (2003) 93.
[97] M.L. Lee, G. Tölg, E. Beinrohr, P. Tschöpel, Anal. Chim. Acta 272 (1993) 193.
[98] J.G. Sen Gupta, Talanta 36 (1989) 651.
[99] H. Niskavaara, E. Kontas, Anal. Chim. Acta 231 (1990) 273.
[100] E. Adriaenssens, P. Knoop, Anal. Chim. Acta 68 (1974) 37.
[101] G.L. Everett, Analyst 101 (1976) 348.
[102] M.E. Farrago, P.J. Parsons, Analyst 107 (1982) 1218.
[103] Y. Zhong, X. Zeng, C. Wang, Guangpuxue Guangpu Fenxi 8 (1988) 55.
[104] M.R.A. Michaelis, W. Wegscheider, H.M. Ortner, J. Anal. Atom. Spectrosc. 3 (1988) 503.
[105] K. Li, B. Xin, X. Chen, Fenxi Huaxue 16 (1988) 603.
[106] M. Bergeron, M. Beaumier, A. Hebert, Analyst 116 (1991) 1019.
[107] N.K. Bel'skii, L.A. Nebol'sina, L.K. Shubochkin, Zav. Labor. 55 (1989) 49.
[108] G. Schmiedel, E. Mainka, Fresen. Zh. Anal. Chem. 335 (1989) 195.
[109] M.R. Winchester, S.M. Hayes, R.K. Marcus, Spectrochim. Acta, Part B 46 (1991) 615.
[110] P. Vest, M. Schuster, K.H. Konig, Fresen. J. Anal. Chem. 339 (1991) 142.
[111] H. Xiao, S. Liang, Fenxi Shiyanshi 13 (1994) 31.
[112] C. Bao, K. Zhang, Q. Sun, Fenxi Huaxue 22 (1994) 179.
[113] N.K. Bel'skii, L.A. Nebol'sina, L.K. Shubochkin, Zh. Anal. Khim. 37 (1982) 61.
[114] N.K. Bel'skii, L.A. Nebol'sina, L.K. Shubochkin, Nov. Metody Spektrosk. Anal. (1983) 118.
[115] P.J. Aruscavage, F.O. Simon, R. Moore, Geostandard Newslett. 8 (1984) 3.
[116] R. Boisvert, M. Bergeron, J. Turcotte, Anal. Chim. Acta 246 (1991) 365.
[117] E.B. Stavnivenko, I.V. Kubrakova, N.I. Shcherbinina, G.V. Myasoedova, N.M. Kuz'min, J. Anal. Chem. 50 (1995) 1136.
[118] L. Kulikova, O. Shiryaeva, Y. Karpov, Latvijas Kkimijas Z. 2 (2003) 154.
[119] Z. Aneva, S. Arpadjan, I. Kalaidjieva, Anal. Chim. Acta 236 (1990) 385.
[120] J. Amossé, W. Fischer, M. Allibert, M. Piboule, Analusis 14 (1986) 26.
[121] R. Eller, F. Alt, G. Toelg, H.J. Tobschall, Fresen. Zh. Anal. Chem. 334 (1989) 723.
[122] I.V. Kubrakova, G.M. Varshal, E.M. Sedykh, G.V. Myasoedova, I.I. Antokol'skaya, T.P. Shemarykina, Zh. Anal. Khim. 38 (1983) 2205.
[123] I. Rubeska, Chem. Lysty 84 (1990) 250.
[124] H. Matusiewicz, M. Lesinski, Int. J. Environ. Anal. Chem. 82 (2002) 207.
[125] H. Matusiewicz, M. Lesinski, Chem. Inz. Ekologiczna 10 (2003) 87.
[126] V.V. Belova, A.A. Vasil'eva, N.V. Androsova, Zav. Labor. 48 (1982) 32.
[127] J. Haines, R.V.D. Robert, S. Afr. J. Chem. 37 (1984) 121.
[128] X. Cui, H. Ma, Bandaoti Xuebao 9 (1988) 129.
[129] H. Zhang, X. Cheng, Fenxi Huaxue 24 (1996) 121.
[130] A.A. Vasil'eva, T.M. Korda, V.G. Torgov, A.N. Tatarchuk, Zh. Anal. Khim. 46 (1991) 1293.
[131] B.V. L'vov, L.A. Pelieva, E.K. Mandrazhi, S.K. Kalinin, Zav. Labor. 45 (1979) 1098.
[132] N.A. Borshch, Y.A. Zolotov, L.N. Kolonina, O.M. Petrukhin, V.N. Shevchenko, O.A. Shiryaeva, Zh. Anal. Khim. 35 (1980) 2369.
[133] O.A. Shiryaeva, L.N. Kolonina, I.N. Vladimisrkaya, V.A. Shestakov, G.I. Malofeeva, O.M. Petrukhin, Y.A. Zolotov, E.V. Marcheva, Y.I. Murinov, Y.E. Nikitin, Zh. Anal. Khim. 37 (1982) 281.
[134] T. Paukert, I. Rubeska, Anal. Chim. Acta 278 (1993) 125.
[135] I.V. Kubrakova, T.F. Kudinova, N.M. Kuzmin, I.A. Kovalev, G.I. Tsysin, Y.A. Zolotov, Anal. Chim. Acta 334 (1996) 167.
[136] F. Zereini, H. Urban, Emissionen Platinmetallen (1999) 97.
[137] U. Oppermann, E. Canu, Labor-Fachzeitschrift 48 (2004) 204.
[138] G.V. Myasoedova, I.I. Antokol'skaya, I.V. Kubrakova, E.V. Belova, M.S. Mezhirov, G.M. Varshal, O.N. Grishina, N.G. Zhukova, F.I. Danilova, S.B. Savvin, Zh. Anal. Khim. 41 (1986) 1816.
[139] V.C. Torgov, M.G. Demidova, T.M. Korda, N.K. Kalish, R.S. Shulman, Analyst 121 (1996) 489.

[140] W.B. Rowston, J.M. Ottaway, Analyst 104 (1979) 645.

[141] J.G. Sen Gupta, Talanta 40 (1993) 791.

[142] Y. Chen, Yanshi Kuangwu Ceshi 4 (1985) 357.

[143] V.N. Mitkin, S.B. Zayakina, V.G. Tsimbalist, A.A. Galizky, Spectrochim. Acta, Part B 58 (2003) 297.

[144] V.N. Mitkin, S.B. Zayakina, G.N. Anoshin, Spectrochim. Acta, Part B 58 (2003) 311.

[145] K. Ohta, J. Ogawa, T. Mizuno, Analusis 25 (1997) 1.

[146] G. Rossi, N. Omenetto, G. Pigozzi, R. Vivian, U. Mattiuz, F. Mousty, G. Crabi, Atom. Spectrosc. 4 (1983) 113.

[147] E. Ivanova, N. Iordanov, I. Khavezov, M. Stoimenova, S. Kadieva, Fresen. J. Anal. Chem. 336 (1990) 501.

[148] E.M. Sedykh, G.V. Myasoedova, G.R. Ishmiyarova, O.G. Kasimova, Zh. Anal. Khim. 45 (1990) 1895.