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Simultaneous determination of rhodium and ruthenium by high-resolution continuum source graphite furnace atomic absorption spectrometry

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ABSTRACT

In the present paper a fast, simple and sensitive analytical method for simultaneous determination of rhodium and ruthenium by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) was developed. Among six pairs of absorption atomic lines of Rh and Ru, which are close enough to enable their simultaneous detection, two pairs were selected for further studies. Best results were obtained for measurements of the resonance line of rhodium at 343.489 nm and the adjacent secondary line of ruthenium at 343.674 nm (23% intensity of this line). For evaluated lines, the absorbance values were obtained using three pixels. The pyrolysis and atomization temperatures were 1200 °C and 2600 °C, respectively. Under these conditions the limits of detection achieved for Rh and Ru were found to be 1.0 μg L^{-1} and 1.9 μg L^{-1}, respectively. The characteristic mass was 12.9 pg for Rh and 71.7 pg for Ru. Repeatability of the results expressed as a relative standard deviation was typically below 6%.

The trueness of the method was confirmed by analysis of the certified reference material – platinum ore (SARM 76). The recovery of Rh and Ru from the platinum ore was 93.0 ± 4.6% and 90.1 ± 2.5%, respectively. The method was successfully applied to the direct simultaneous determination of trace amounts of rhodium and ruthenium in spiked river water, road runoff, and municipal sewage. Separation of interfering matrix on cation exchange resin was required before analysis of road dust and tunnel dust (CW-7) by HR-CS GFAAS.

1. Introduction

Rhodium and ruthenium, which are members of Platinum Group Metals (PGMs), naturally occur at trace concentration in the environment (1 μg kg^{-1} in the Earth's crust and 1 ng kg^{-1} in seawater) [1]. Due to their unique physical and chemical properties, such as high melting temperature, inertness towards many chemical reagents, extreme hardness, good conductivity, and excellent catalytic properties, both elements have been widely used in a number of applications, e.g. automotive, glass, chemical and engineering industries [1,2]. Ruthenium, which is also classified as a “green minor metal”, is very important in terms of green energy technologies (i.e. solar energy, fuel cells, light emitting diodes) [3].

In 2015 the total world demand of rhodium and ruthenium reached 30.8 tons and 29 tons, respectively [4]. Most of the production of both metals was consumed in the manufacturing of automobile-exhaust emission control catalysts and electrical contacts used in the production of electronic equipment. Such electronic devices contain precious metals with concentrations 40 to 50 times more abundant than naturally occurring deposits [5]. The rapid growth in electronic industry and drastic decrease in the product's lifetime mean that more and more consumers replace electronic equipment. Increasing number of cars, equipped with catalytic converters, and exponential growth of electronic waste (e-waste), results in raising of rhodium and ruthenium content in the environment and generates the need to develop an efficient and cheap analytical procedures, enabling fast determination of these elements in real samples. The content of rhodium and ruthenium in different environmental samples, such as surface and sea waters, sewage sludge, road dust, and soil, has been found in the range of 0.2–102 μg kg^{-1} for Rh and 0.01–28 μg kg^{-1} for Ru [6,7]. The highest content of Rh was reported in road dust collected in Beijing (China) (97 μg kg^{-1}) [8], Huston (Texas, USA) (204 μg kg^{-1}) [9] and Jerusalem (Israel) (450 μg kg^{-1}) [10]. The content of Ru found in sewage sludge in the United Kingdom was in the range 3–28 μg kg^{-1}, but in raw incinerator ash from the sewage treatment facilities reached even 100 μg kg^{-1}, while during storage its content decreased to 12–45 μg kg^{-1} [7].

The simultaneous determination of Rh and Ru is a matter of scientific and practical interest due to the fact that these metals occur together in many environmental and industrial (catalysts, e-wastes) samples. A multi-element analytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled

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plasma mass spectrometry (ICP MS) have been often used for simultaneous analysis of PGMs in environmental samples [1,2,11,12], but their application for determination of ruthenium is less common. A survey of literature indicates that only a few papers have been published on the simultaneous determination of Rh and Ru at trace level in vehicle escape fumes [13], stream sediment, plant leaves [14] and road dust (CRM BCR-723) [14,15]. Both elements have been also determined simultaneously in platinum ore (CRM SARM 7) [14] and geological reference materials (TDB-1, WGB-1, UMT-1, WMG-1, SARM-7) [15] after microwave-assisted acid digestion. In many cases, matrix components of the samples cause a spectral and non-spectral interferences which hinder determination of Rh and Ru [2,11,14,16,17]. For this reason, analytical procedures used for the determination of PGMs include microwave digestion, separation and/or preconcentration steps [11,18,19]. It is worth mentioning, that combination of microwave digestion and atomic absorption spectrometry is a very rapid and relatively cheap method for PGMs analysis in a large number of environmental samples containing PGMs at the level of mg kg^{-1} [11,20,21].

During the past decade, the potential of a new spectrometric technique – high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) to perform simultaneous determination of two or more elements in different kind of samples was demonstrated [18]. HR-CS AAS spectrometer provides exceptional resolution and enables monitoring of a portion of the spectrum (about 0.3 nm for the UV region up to 0.5 nm for the visible region), in which several lines may be measured at the same time. Monitoring the spectral neighborhood of the analyte lines permits to detect easily potential spectral interferences and to determine two or more elements simultaneously [22,23]. The HR-CS GFAAS technique have been explored frequently for simultaneous determination of several transition elements possessing many analytical lines and similar thermal behavior, such as Cr and Fe [24], Ni and V [25], Ni and Co [26], Co, Al and Fe [27], Fe and Cd [28], Sn, Fe and Cd [29] as well as Mo and Ni [30] in various digested samples (Table 1). Using of solid sampling HR-CS GFAAS allowed to overcome spectral interferences during simultaneous determination of Mo and Ni soil [30] and plants [31]. Resano et al. [32] used this technique for direct monitoring of Pt and Rh in de-activated automotive catalysts as well as Pd and Rh, Pt and Rh in pharmaceutical ingredients. The used closely adjacent atomic lines were: 244.006 nm for Pt and 244.034 nm for Rh ($\Delta\lambda = 0.028$ nm) as well as 360.955 nm for Pd and 361.247 nm for Rh ($\Delta\lambda = 0.292$ nm). The simultaneous atomization of elements from powdered samples (1–5 mg) was performed at 2600 °C using ammonium hydrogen difluoride solution (($NH_4F \cdot HF$) as modifier.

The goal of this work was to develop a new analytical method for the simultaneous determination of Rh and Ru by HR-CS GFAAS. For this purpose, the spectral lines of Rh at 343.489 nm and Ru at 343.674 nm were selected and the measurement parameters were optimized. Figures of merit of the method, such as linear range of calibration curves, sensitivity, selectivity, limit of detection, and precision were evaluated. The accuracy of the method was proved by analysis of spiked samples and certified reference material (CRM SARM 76). The method was applied for the simultaneous determination of trace amounts of rhodium and ruthenium in environmental and geological samples.

2. Experimental

2.1. Instrumentation and measurements conditions

All the absorption measurements were performed using a high-resolution continuum source atomic absorption spectrometer ContrAA® 700 (Analytik Jena AG, Jena, Germany) equipped with a transversely heated graphite tube atomizer and AS-GF autosampler. Measurements were carried out using 20 μL of the sample solution and pyrolytically coated standard tubes (Analytic Jena, Part No.: 407-A81.011). The optical system comprises continuum light source 300 W high-pressure xenon short-arc lamp XBO 301 (GLE, Berlin, Germany) operating in a “hot-spot” mode, suitable for all elements determination in the wavelength range from 185 nm to 900 nm. The spectrometer consists of a high-resolution compact double monochromator and a linear charge-coupled device (CCD) array detector with 588 pixels. The detector allows for visualization of the environment of the analytical line using 200 pixels, while the rest are used for internal function, such as correcting for fluctuations in the lamp intensity.

Two pairs of the analytical lines of rhodium and ruthenium: 343.489 nm for Rh and 343.674 nm for Ru as well as 349.873 nm for Rh and 349.895 nm for Ru were chosen for simultaneous determination

Table 1
Literature data on the simultaneous determination of metals by HR-CS GFAAS.

Techniqe	Analyte	Wavelength, nm	Relative sensitivity, %	Number of pixels	LOD	RSD, %	Sample	Chemical modifier	Ref.
HR-CS GFAAS	Ni	305.432	2.8	3	3.0 mg kg^{-1}	4.3-8.0	Crude Oil	HNO_3 + Triton X-100	25
	V	305.633	20	3	1.0 mg kg^{-1}	0.1- 9.0			
	Cr	357.868	100	3	0.001 mg kg^{-1}	6.0-20	Crude Oil	No modifier	24
	Fe	358.120	1	3	0.600 mg kg^{-1}	4.0-16			
	Ni	231.096	59	9	0.390 μg L^{-1}	0.2-4.2	Formulations of vitamin B12	No modifier	26
	Co	231.136	0.11	9	1210 μg L^{-1}	0.8-10			
	Co	237.185 + 237.283 + 237.386	0.43 + 0.2 + 0.038	3	12.0 μg L^{-1}	3.1-8.7	CRM: NCS ZC 73016, NCS ZC 73013, SRM NIST 1643e, waste water	No modifier	27
	Al	237.312	43	3	14.0 μg L^{-1}	0.7-6.7			
	Fe	237.362	0.83	3	16.0 μg L^{-1}	0.3-4.0			
	Sn	228.668	2.9	5	0.06 μg L^{-1}	5.3-6.8	Canned peeled tomato, canned sardine, SRM NIST 1515	0.1% Pd + 0.05% Mg in 0.5% HNO_3	29
	Fe	228.725	0.91	5	0.04 μg L^{-1}	4.0-6.8			
	Cd	228.802	100	3	0.04 μg L^{-1}	3.4-4.7			
	Fe	228.725	0.91	3	0.03 mg kg^{-1}	2.4-13	Industrial sewage, sewage sludge	5 μg Pd	28
	Cd	228.802	100		90.0 mg kg^{-1}	0.3-20			
	Mo	313.259	100	3	0.05 μg L^{-1}	1.2-3.3	Wine	0.5 mg of $NH_4H_2PO_4$ in 0.05% Triton X-100	30
	Ni	313.410	4.8	3	0.81 μg L^{-1}	1.1-5.1			
HR-CS SS GFAAS	Pt	244.006	19	3	8.3 mg kg^{-1}	3.0-11	Automobile catalysts	4% $NH_4F \cdot HF$	32
	Rh	244.034	4.8	3	9.3 mg kg^{-1}				
	Pd	360.955	7.7	3	0.08 mg kg^{-1}	2.0-10	Active pharmaceutical ingredients	No modifier	32
	Rh	361.247	2.2	3	0.26 mg kg^{-1}				
	Pt	244.006	19	3	0.15 mg kg^{-1}	2.0-10	Active pharmaceutical ingredients		32
	Rh	244.034	4.8	3	0.10 mg kg^{-1}				

LOD – limit of detection, RSD – relative standard deviation, CRM – certified reference material, SRM – standard reference material, NCS ZC 73016 – chicken, NCS ZC 73013 – spinach, SRM NIST 1643e – trace elements in water, SRM NIST 1515 – apple leaves, CW-7 – tunnel dust, SARM 76 – platinum ore, SS – solid sampling.