Rhodium

Application	Determination in urine and serum/plasma
Analytical principle	Adsorptive voltammetry
Completed in	September 1999

Summary

The method presented here permits the reliable determination of rhodium in urine down to the lower ng per litre range. However, determination of physiological rhodium excreted in urine is not possible using this method. The urine sample is mineralised either by high-pressure digestion (HPA) or UV digestion. Formaldehyde solution is added to the digestion solution for the purpose of forming a complex with rhodium. This complex is enriched by adsorption on a hanging mercury drop electrode (HMDE) within a defined period at a potential of –0.7 V. When the voltage is subsequently shifted in the cathodic direction in the differential pulse mode a current peak occurs at approximately –1.12 V. The height of this peak is directly proportional to the rhodium concentration. Evaluation is carried out using the standard addition procedure.

Within-series imprecision: Urine, spiked (high-pressure digestion, urine volume 5 mL)
Standard deviation (rel.) s_w = 16.0%
Prognostic range u = 36.2%
at a concentration of 10 ng rhodium per litre urine
and where n = 10 determinations

Urine, spiked (UV digestion, urine volume 1 mL)
Standard deviation (rel.) s_w = 6.0%
Prognostic range u =13.6%
at a concentration of 10 ng rhodium per litre urine
and where n =10 determinations

Between-day imprecision: Urine, spiked (UV digestion, urine volume 1 mL)
Standard deviation (rel.) s = 8.1%
Prognostic range u = 18.3%
at a concentration of 10 ng rhodium per litre urine
and where n = 10 days

Accuracy:	Urine, spiked (high-pressure digestion, urine volume 5 mL) Recovery rate r = 87–116% at a concentration of 10 ng rhodium per litre urine and where n = 10 determinations
	Urine, spiked (UV digestion, urine volume 1 mL) Recovery rate r = 85–100% at a concentration of 10 ng rhodium per litre urine and where n = 10 determinations
Detection limit:	1.0 ng rhodium per litre urine (high-pressure digestion, urine volume 5 mL) 5.0 ng rhodium per litre urine (UV digestion, urine volume 1 mL)

Rhodium

Metallic rhodium (Rh: atomic number 45, rel. atomic weight 102.9) belongs to the platinum group of elements and as such it exhibits the typical properties and relationships of this group.

Rhodium is a silvery white, tough, ductile and forgeable metal. It generally occurs in its most important oxidation state +III, but all the other states up to +VI are known. Rhodium and its compounds are of particular importance as catalysts. Thus rhodium(III) chloride ($RhCl_3$) serves as a catalyst in reduction reactions, polymerisations, isomerisations and other chemical syntheses. Rhodium forms complexes with carbon monoxide, triphenylphosphine, tetracyanoethylene, amines and other ligands. These complexes, such as the so-called Wilkinson's catalyst [chlorotris(triphenylphosphine) rhodium(I), $RhCl[P(C_6H_5)_3]_3$], can be used as catalysts in homogeneous systems, e.g. for carbonylation (Monsanto acetic acid process) and decarbonylations, hydroformulations and oxidations [1]. In the meantime rhodium is increasingly used in automobile catalytic converters, e.g. such as the three-way catalytic converters commonly mounted on cars in Germany [2]. When rhodium is used for this purpose it must be expected that a certain amount of metallic or oxidised rhodium will be expelled into the environment.

The most important route of human intake of rhodium is presumably the ingestion of dust containing traces of rhodium. In addition, inhalation of dust particles can play a certain role. The excretion of rhodium in urine associated with environmental exposure is below 1 ng/L in man [3]. Currently, carcinogenic and sensitising effects are under discussion as possible consequences of chronic exposure to small doses of rhodium.

However, the carcinogenic potential of rhodium compounds cannot be finally assessed, as insufficient data is as yet available. At present it is not clear if, as in the case of platinum, the trivalent, hexagonal rhodium complexes possess carcinogenic properties, because it has been shown that Rh(I) and Rh(II) organo-complexes also have

antitumourigenic effects [4]. The TLV value in the USA (1999) is 1 mg/m^3 for insoluble rhodium compounds and metallic rhodium, and 0.01 mg/m^3 for soluble rhodium compounds. These limits were set especially to prevent irritation of the skin and the mucous membranes. Rhodium and its compounds were assigned to group A4 of the carcinogenic working materials and rated "not classifiable as a human carcinogen" by the American Conference of Governmental Industrial Hygienists. This indicates that, though there are grounds for concern that rhodium and its compounds may have a carcinogenic effect on humans, no conclusive evaluation can be made at present due to insufficient information [5].

Recently seven employees of an automobile catalytic converter recycling plant were examined for rhodium excretion in their urine as part of a study in occupational medicine (cf. Table 1) [3].

Table 1. Rhodium excretion in the urine of seven employees of an automobile catalytic converter recycling plant.

Test Subject No.	Rhodium concentration in urine [ng/L]
1	13
2	6
3	29
4	82
5	16
6	12
7	2

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Contents

1 General principles

The urine sample is mineralised either by high-pressure digestion (HPA) or UV digestion. Formaldehyde solution is added to the digestion solution for the purpose of forming a complex with rhodium. This complex is enriched by adsorption on a hanging mercury drop electrode (HMDE) within a defined period at a potential of –0.7 V. When the voltage is subsequently shifted in the cathodic direction in the differential pulse mode, a current peak occurs at approximately –1.12 V. The height of this peak is directly

proportional to the rhodium concentration. Evaluation is carried out using the standard addition procedure.

2 Equipment, chemicals and solutions

2.1 Equipment

High pressure ashing device with 70 mL digestion vessels made of quartz glass (e.g. HPA®, from H. Kürner, Rosenheim)

Heating block made of aluminium with drilled slots to accommodate the 70 mL digestion vessels

UV digestion device with 12 mL digestion vessels made of quartz glass (e.g. from Metrohm)

Differential pulse polarograph (e.g. from Metrohm)

Inverse voltammetric measuring cell with gas inlet, hanging mercury drop electrode (HMDE), glassy carbon auxiliary electrode, reference electrode (Ag/AgCl/3 M KCl) and synchronous stirrer (e.g. from Metrohm)

Control unit for the voltammetric pre-enrichment (e.g. from Metrohm)

Microlitre pipettes, adjustable between 10 and 100 µL, and between 100 and 1000 µL (e.g. from Eppendorf)

Millilitre pipette, adjustable between 1 and 10 mL (e.g. Varipette from Eppendorf)

10, 100 and 1000 mL Volumetric flasks

100 mL Graduated cylinder

25 mL Glass beaker

2.2 Chemicals

Rhodium standard solution (1.0 g/L) in 10% hydrochloric acid (e.g. from Aldrich)

65% Nitric acid (e.g. Suprapur, from Merck)

37% Hydrochloric acid p.a. (e.g. from Merck)

96% Sulphuric acid p.a. (e.g. from Merck)

Hydrogen peroxide (e.g. Suprapur, from Merck)

37% Formaldehyde solution, stabilised with 10% methanol p.a. (e.g. from Merck)

Ultrapure water (equivalent to ASTM type 1; R >15 MW/cm)

Nitrogen (at least 99.99%).

2.3 Solutions

0.42 M Hydrochloric acid:
Approx. 600 mL ultrapure water are placed in a 1000 mL volumetric flask. Then 35 mL 37% hydrochloric acid are added using a 100 mL graduated cylinder and the flask is filled to its nominal value with ultrapure water.

3.7% Formaldehyde solution:
1 mL of the 37% formaldehyde solution is placed in a 25 mL glass beaker and diluted with 9 mL ultrapure water. This solution must be freshly prepared every day.

2.4 Calibration standard

Stock solution (1 mg/L):
100 µL of the rhodium standard solution (1.0 g/L) are pipetted into a 100 mL volumetric flask. The volumetric flask is then filled to its nominal volume with 0.42 M hydrochloric acid. The stock solution can be stored for approx. 2 weeks.

Standard addition solution (1 µg/L):
100 µL of the stock solution (1 mg/L) are pipetted into a 100 mL volumetric flask.
The volumetric flask is then filled to its nominal volume with 0.42 M hydrochloric acid.
This solution must be freshly prepared every day.

3 Specimen collection and sample preparation

As is the case for all trace element analyses, it is essential to ensure that the reagents are of the highest possible purity and that the vessels are thoroughly clean. This also applies to sample collection.

To prevent any possible exogenous contamination, each of the plastic vessels for sample collection must be cleaned before use by leaving them filled with 1% nitric acid for at least 2 hours, rinsing them thoroughly with ultrapure water and drying them.

For determination in the range of the detection limit the cleansing effect can be improved by warming the nitric acid.

The urine should be collected and stored in polyethylene vessels. If the determination cannot be carried out immediately, the urine can be stored in the refrigerator for 1 week at approximately + 4°C, but the urine must be acidified (approx. 1 mL glacial acetic acid per 100 mL urine). If longer storage is necessary, it is advisable to keep the samples in the deep-freezer at approx. –18°C.

The urine samples are thawed and brought to room temperature for further processing. To obtain correct analytical results it is essential to ensure that the urine sample is homogeneous. If sediment has formed, the sample is to be warmed to try and dissolve the sediment. If necessary, the sample must be carefully shaken before being divided into aliquots to ensure that any residual precipitate is distributed as homogeneously as possible.

3.1 High-pressure digestion (HPA)

5 mL of urine are pipetted into the 70 mL quartz glass vessels of the high-pressure digestion device and reduced to approx. 1 mL in the heating block. Then 4 mL 65% nitric acid and 0.5 mL 37% hydrochloric acid are added. The vessels are sealed according to instructions and placed in the high-pressure digestion device.

The samples thus prepared are mineralised according to the following temperature programme:

Programme step	Time [min]	Temperature [°C]
1	40	from 20 to 320
2	60	320
cooling	approx. 120	from 320 to 20

After opening the vessel, 100 µL 96% sulphuric acid are added. The mixture is reduced to a volume of approx. 0.1 mL in the heating block at a maximum temperature of 160–170 °C. The complete expulsion of the nitric acid is achieved by repeated addition of 37% hydrochloric acid (0.5 mL) and reduction of the volume to approx. 0.1 mL in each case. After the last addition of hydrochloric acid, no more formation of nitrogen oxides may be observed. A reagent blank is included in the whole digestion process, whereby ultrapure water is subjected to the entire sample preparation instead of urine.

3.2 UV digestion

In each case 1 mL of urine, 100 µL 96% sulphuric acid, 200 µL hydrogen peroxide and 5 mL ultrapure water are pipetted into the digestion vessels. After mixing, the vessels are placed into the UV digestion device and irradiated for approx. 3 h with UV light at a

maximum temperature of 93 °C. The colourless solutions are subsequently brought to room temperature.

A reagent blank is included in each analytical series. Ultrapure water is used instead of urine in this case.

4 Operational parameters for adsorptive inverse voltammetry (DPP)

Working electrode:	Hanging mercury drop electrode (HMDE), drop size 3 (VA Stand from Metrohm)
Reference electrode:	Ag/AgCl/3M KCl
Auxiliary electrode:	Glassy carbon
Duration of nitrogen purging:	5 minutes
Pre-electrolysis potential:	–0.7 V
Pre-electrolysis duration:	120 s while stirring (2000 rpm) 10 s without stirring
Scan speed:	10 mV/s
Trigger:	0.5 s
Voltage range:	–0.7 V to –1.3 V
Pulse amplitude:	–50 mV
Sensitivity:	10 nA/mm (depending on the Rh concentration)
Temperature:	Room temperature

5 Analytical determination

The digested solutions prepared as described in Sections 3.1 or 3.2 are completely transferred with 0.42 M HCl into the voltammetric measuring vessel, whereby the final volume of the assay solution is approx. 10 mL or 15 mL, depending on the size of the vessel. It is important to ensure that all the electrodes and the nitrogen inlet are immersed in the assay solution. Now 100 µL 3.7% formaldehyde solution are added to form a complex with the rhodium. Nitrogen is passed through the assay solution for 5 minutes to purge it from any dissolved oxygen, and then the current-voltage curve is recorded twice under the operational conditions described above. Ideally, both curves should be congruent.

6 Calibration

Calibration is carried out by adding the standard addition solution (1 µg/L) to the original assay solution and repeating the voltammetric determination. This procedure must be repeated at least three times. For this purpose an aliquot of 20 µL of the standard addition solution containing 1 µg rhodium per litre (equivalent to 20 pg rhodium) is added to the assay solution three times. Each addition is equivalent to a concentration increase of 4 ng per litre based on the volume of urine used (5 mL) or 20 ng per litre based on a urine volume of 1 mL. Automatic dosing devices have proved particularly useful for standard addition. The change in volume of the assay solution due to addition of the standard addition solution (3 times 20 µL) is less than 1% and is thus negligible (see also Section 7).

The given standard additions are applicable for rhodium concentrations of 4 ng per litre urine (urine volume 5 mL) or 20 ng per litre urine (urine volume 1 mL). If other concentrations of rhodium are present in urine, the concentration of the standard additions must be chosen so that the signal of the assay solution is approximately doubled as a result of an addition.

Based on a urine volume of 5 mL, the calibration curve is linear up to a concentration of 100 ng rhodium pro litre urine. Based on a urine volume of 1 mL, the linear range of the calibration curve extends to 500 ng rhodium per litre urine.

7 Calculation of the analytical result

The rhodium content in the assay solution is preferably determined by means of the height of the current peak in a graph. The height of the current peak (in mm or nA) is plotted as a function of the added amount of rhodium, taking any possible reagent blank value into consideration (Fig. 1). The basis for the graphic evaluation is the horizontal extension of the baseline immediately before it rises to the peak. The heights of the current peaks (in mm or nA) are plotted versus the added amounts of rhodium (e.g. 0, 20, 40, 60 pg), whereby any blank value must be taken into account (cf. Fig. 2). The rhodium content of the sample in pg is the point at which the best-fit straight line intersects with the abscissa. To obtain the concentration this value must be divided by the sample volume used (e.g. pg/mL = ng/L).

If the change in volume of the sample solution caused by the added standard is less than 1% (this is the case in this method), the resulting concentration change can be considered as negligible for the calculation. The deviation of the measured values for the standard addition solutions from the best-fit straight line gives an indication of the quality of the determination. Individual erroneous measurements can be readily recognised. Evaluation can also be carried out by a linear regression calculation. In any case, however, the results should be plotted graphically as well.

8 Standardisation and quality control

Quality control of the analytical results is carried out as stipulated in the guidelines of the Bundesarztekammer (German Medical Association) [6, 7] and in the special preliminary remarks to this series.

As no reference material for rhodium is commercially available, it must be prepared in-house in the laboratory. For this purpose, urine is spiked with a defined quantity of rhodium. Aliquots of this solution can be stored in the deep-freezer for up to a year and used for quality control. The concentration of this control material should lie in the middle of the most frequently occurring concentration range. The expected value and the tolerance range of this quality control material are ascertained in a pre-analytical period (one analysis of the control material on each of 20 different days) [6, 8].

9 Reliability of the method

9.1 Precision

In order to determine the precision in the series, a urine sample of a person who had not been exposed to rhodium at the workplace was spiked with rhodium so that a concentration of 10 ng per litre urine resulted. This sample (5 mL in each case) was subsequently processed and analysed 10 times (HPA). The standard deviation of the results was 16%, which is equivalent to a prognostic range of 36.2%. In addition, this sample (1 mL in each case) was subsequently processed and analysed 10 times (UV digestion). The standard deviation of the results was 6.0%, which is equivalent to a prognostic range of 13.6%.

In order to determine the precision from day to day, 1 mL of the urine sample described above was processed and analysed on 10 different days (UV digestion). The standard deviation of the results was 8.1%, which is equivalent to a prognostic range of 18.3%.

9.2 Accuracy

Recovery experiments were performed to determine the accuracy of the method. For this purpose 1 mL (UV digestion) or 5 mL (HPA) of the sample used to determine the precision was processed and analysed 10 times in each case. The recovery rate was between 87 and 116% in the case of the HDA digestion and between 85.0 and 100% for digestion with UV light.

9.3 Detection limit

The detection limit, determined as three times the standard deviation of the reagent blank value, is 1.0 ng rhodium per litre urine (high-pressure digestion, 5 mL urine) or 5 ng rhodium per litre urine (UV digestion, 1 mL urine).

9.4 Sources of error

This is an extremely sensitive method which can detect the analyte in the ultratrace range (ppt range). Accordingly, the analysis must be carried out with care. It is especially important to check the reagents and vessels used for possible rhodium contamination.

In general, surface-active substances interfere with adsorptive voltammetric determinations, as they, like the analyte complex, are adsorbed onto the mercury drop and thus block its surface. Quantitative rhodium determination is no longer possible in this case. Surface-active substances can be contained in the solution, e.g. after incomplete digestion of the biological material. Therefore it must be ensured that the samples are completely mineralised. These conditions are fulfilled by the digestion methods described under Section 3. In the case of the HPA digestion the maximum temperature of 320 °C must definitely be reached, as the oxidation potential of the nitric acid is only then sufficient to achieve complete mineralisation. The digested sample solutions must be clear and colourless.

In the case of the HPA digestion the excess nitric acid causes considerable interference with the inverse voltammetric determination of rhodium. It must therefore be expelled by heating with hydrochloric acid after the actual digestion is complete. Therefore, the instructions on time and temperature must be followed exactly, otherwise rhodium loss can result. The urine volumes given here (5 mL for HPA digestion and 1 mL for UV digestion) represent the upper limits at which optimum sensitivity (detection limit) of the method is achieved. Larger amounts can result in matrix interference with the adsorptive voltammetric measurement, as it is possible that complete mineralisation cannot be achieved under these conditions.

Interference from other trace elements (e.g. other metals in the platinum group) has not been observed at concentrations such as those normally present in biological materials.

The time schedule of the adsorptive voltammetric measurement is of critical importance for the reproducibility of the individual measurements. It should be noted that the adsorption of the complex on the electrode occurs even before voltage is applied. Therefore the period between the formation of the mercury drop and the beginning of the pre-electrolytic enrichment must be exactly defined and kept constant in each case. Furthermore, the size of the drop, and thus the size of the adsorbent mercury surface, is significant. The best results are obtained only with automatically controlled devices.

The risk of contamination of the assay sample from the vessels and reagents used is relatively low. No blank value due to the reagents used has been observed.

The increasing use of catalytic converters in automobiles has led to a rise in the rhodium content in ubiquitous dust. Therefore contamination of the sample material from the time of its collection until the determination is carried out must be avoided at all cost.

When HPA is used it is important to note that memory effects can occur in the digestion vessels after the digestion of samples with a higher content of rhodium and when digestion residues are present (e.g. samples containing silicate). It is difficult to eliminate these effects even by careful cleaning (e.g. by steaming them with nitric acid and hydrochloric acid). Thus a blank value is to be expected when vessels are frequently

used. Any digestion residues can be treated for 1 min in an ultrasound bath with cold hydrofluoric acid. A cleansing digestion with nitric acid and hydrochloric acid must be subsequently carried out.

10 Discussion of the method

The conditions described in this present method have been optimised for the determination of rhodium. The procedure is based on a publication by Hong et al. [9], which describes the determination of ultratraces of rhodium in the form of a formaldehyde complex in aqueous systems by means of adsorptive voltammetry. Measurements in real matrices (urine, plant material, tunnel dust) can be carried out for the first time using this method [10, 11].

Platinum does not cause a current peak under these conditions of measurement. If the measurement is performed under the conditions for platinum assay, however, (cf. the Platinum method in Analyses of Hazardous Substances in Biological Materials, Volume 4 [12]), both elements can be determined simultaneously, but with reduced sensitivity for rhodium [10, 13].

Other methods for the determination of rhodium are either insufficiently sensitive, e.g. graphite furnace atomic absorption spectrometry, or they are so strongly impeded by matrix effects, e.g. mass spectrometry with induced plasma, that it has not been possible to carry out measurements in real matrices [10].

In the environmentally relevant range rhodium measurements have been published which are associated with the emission of metals belonging to the platinum group by automobile catalytic converters. In these cases either voltammetry after pressure digestion or graphite furnace AAS after docimastic enrichment were used to analyse samples of soil and dust [14, 15].

The described method represents the most sensitive possibility of determining rhodium in biological materials at present. However, the physiological content of rhodium in body fluids cannot be ascertained using this method. The results of preliminary studies for the purpose of orientation in occupational medicine are now available. All in all, the reliability criteria of the method can be described as good.

Instruments used:
Polarecord 626 from Metrohm, Herisau, Switzerland; VA Stand 663 from Metrohm, Herisau, Switzerland; Timer E 608 from Metrohm, Herisau, Switzerland; High Pressure Ashing device (HPA®), from H. Kiirner, Rosenheim, Germany; UV Digester 705 from Metrohm, Herisau, Switzerland

References

[1] *Römpp Chemie Lexikon:* 9th revised and extended edition, Georg Thieme Verlag, Stuttgart, New York (1989).
[2] *Gesellschaft für Strahlen- und Umweltforschung mbH Neuherberg/Forschungszentrum Jülich GmbH:* Interim Report „Edelmetallemissionen", GSF München (1990).
[3] *F. Alt* and *K. H. Schaller et al:* In preparation.
[4] *T. Gebel:* Toxikologisches Gefährdungspotential der Platingruppenelemente Platin, Palladium und Rhodium. In: *F. Zereini* and *F. Alt* (eds.): Emissionen von Platinmetallen, Springer-Verlag, Berlin, Heidelberg, New York, pp. 269–280 (1999).
[5] *ACGIH American Conference of Governmental Industrial Hygenists:* Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, Cincinnati (1998).
[6] *Bundesärztekammer:* Qualitätssicherung der quantitativen Bestimmungen im Laboratorium. Neue Richtlinien der Bundesärztekammer. Dt. Ärztebl. *85,* A699–712 (1988).
[7] *Bundesärztekammer:* Ergänzung der „Richtlinien der Bundesärztekammer zur Qualitätssicherung in medizinischen Laboratorien". Dt. Ärztebl. *91,* C159–161 (1994).
[8] *J. Angerer* and *K.H. Schaller:* Erfahrungen mit der statistischen Qualitätskontrolle im arbeitsmedizinisch-toxikologischen Laboratorium. Arbeitsmed. Sozialmed. Präventivmed. *1,* 33–35 (1977).
[9] *T.-K. Hong, M.-Z. Czae, C. Lee, Y.-S. Kwon* and *M.-J. Hong:* Determination of ultratraces of rhodium by adsorptive voltammetry of formaldehyde complex. Bull. Korean Chem. Soc. *15,* 1035–1037 (1994).
[10] *C. León, H. Emons, P. Ostapczuk* and *K. Hoppstock:* Simultaneous ultratrace determination of platinum and rhodium by cathodic stripping voltammetry. Anal. Chim. Acta *356,* 99–104 (1997).
[11] *K. Hoppstock* and *F. Alt:* Voltammetrische Bestimmung von Platin- und Rhodiumspuren in Umweltkompartimenten und biologischen Materialien. In: *F Zereini and F Alt* (eds.): Emissionen von Platinmetallen, Springer-Verlag Berlin, Heidelberg, New York, pp. 15–25 (1999).
[12] *F. Alt, J. Messerschmidt, M. Fleischer* and *K.H. Schaller:* Platinum. In: *J. Angerer and K.H. Schaller* (eds.): Analyses of Hazardous Substances in Biological Materials, Volume 4. Deutsche Forschungsgemeinschaft, Wiley-VCH Verlag, Weinheim (1994).
[13] *M.-Z. Czae, C. Lee, T.-K. Hong, Y.-S. Kwon* and *M.-J. Hong:* Simultaneous determination of traces of platinum and rhodium by differential pulse polarography. J. Korean Chem. Soc. *39,* 35–39 (1995).
[14] *E. Helmers* and *N. Mergel:* Platinum and rhodium in a polluted environment: studying the emissions of automobile catalysts with emphasis on the application of CSV rhodium analysis. Fresenius J. Anal. Chem. *362,* 522–528 (1998).
[15] *F. Zereini, B. Skerstupp, F. Alt, E. Helmers* and *H. Urban:* Geochemical behaviour of platinum-group elements (PGE) in particulate emissions by automobile exhaust catalysts: experimental results and environmental investigations. Sci. Total Environ. *206,* 137–146 (1997).

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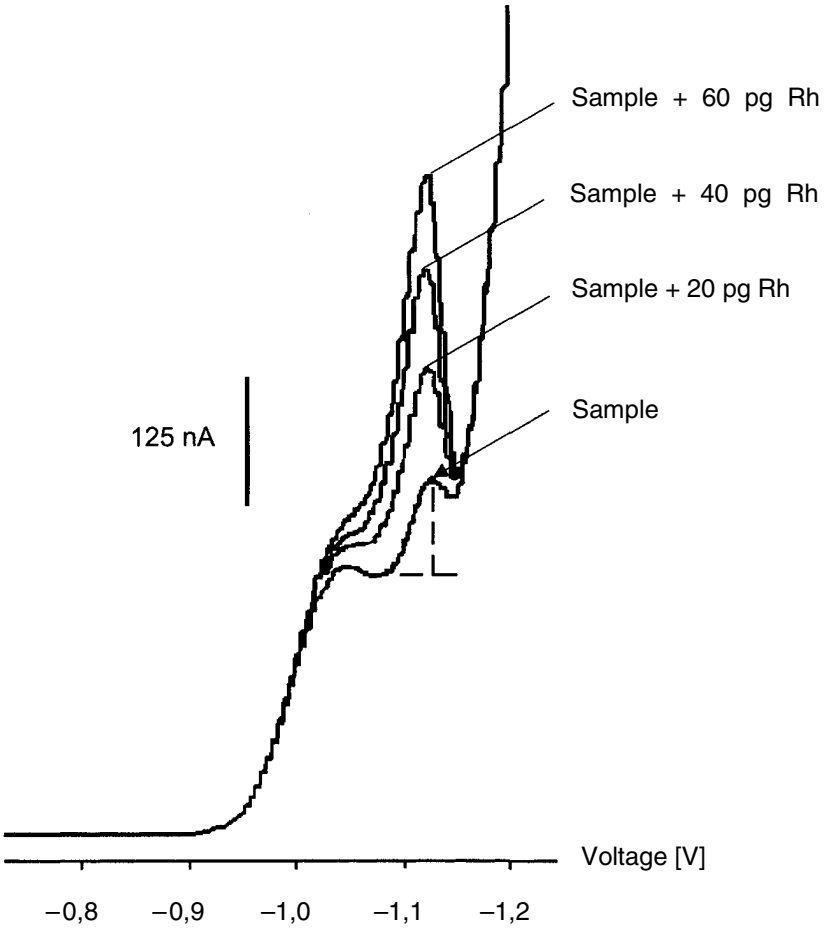

Fig. 1. Recording of the voltammograms in a urine sample spiked with 4 ng/L of rhodium after high-pressure digestion (5 raL urine volume). The sample was spiked with 20, 40 and 60 pg Rh for the quantitative determination.

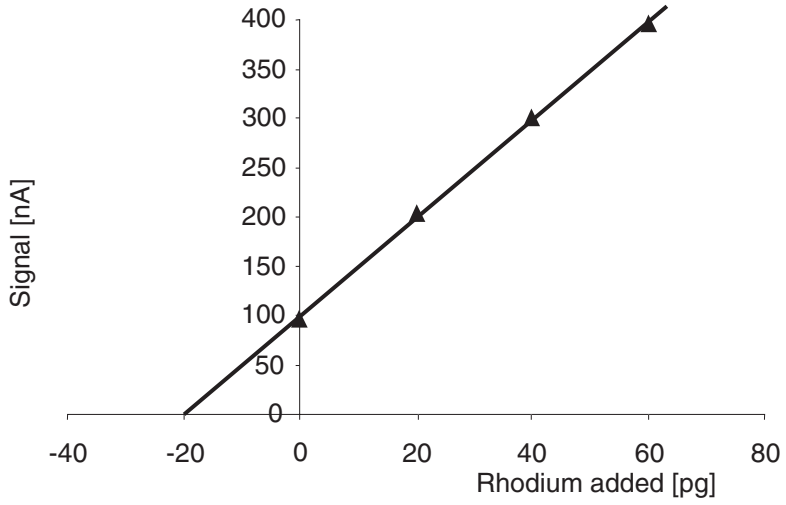

Fig. 2. Graph of a calibration curve for the determination of rhodium in a spiked urine sample (4 ng/L of rhodium, 5 mL urine, HPA digestion).