Vanadium

Application	Determination in urine
Analytical principle	Adsorptive inverse voltammetry (DPP)
Completed in	September 1991

Summary

This analytical method allows reliable determination of vanadium concentrations in urine which result from ecological exposure as well as exposure to vanadium at the workplace. The particular merit of this method is its high sensitivity which surpasses that of ETAAS and ICP/AES by a factor of at least 10.

In order to determine vanadium by adsorptive inverse voltammetry, the biological matrix must be completely eliminated by wet oxidative mineralization. After mineralization, cupferron is added to form a complex with the vanadium in the solution (present in the form of VO^{2+} or VO^{3-}) at pH 8.5. The complex is enriched on a hanging mercury drop electrode (HMDE) at −0.4 V. Then the voltage is changed in the cathodic direction until about −0.95 V. It is advisable to record the current voltage curve using the differential pulse polarography mode (DPP). A current peak occurs at about −0.75 V. This peak is directly proportional to the concentration of vanadium in the assay solution.

Calibration is carried out using the standard addition procedure. Increasing amounts of vanadium are added to the assay solution in small volume increments and the voltammogram is recorded after each addition. The peak height/concentration is linear in the given concentration range.

Within-series imprecision:	Standard deviation (rel.)	s_w = 6.4 %
	Prognostic range	u = 14.0 %
	At a concentration of 2.5 µg vanadium per litre urine and where n = 12 determinations	

Between-day imprecision:	Standard deviation (rel.)	s = 3.9 %
	Prognostic range	u = 10.7 %
	At a concentration of 5 µg vanadium per litre urine and on n = 5 days	
Inaccuracy:	Recovery rate	r = 98 %
Detection limit:	0.2 µg vanadium per litre urine	

Vanadium

Vanadium (atomic number 23, relative atomic mass 50.0415) is a metallic element with a density of 6.0. Its melting point is 1735 °*C* and boiling point 3400 °C. Similar to zinc, 0.014% of the earth's crust is composed of vanadium. It occurs in about 68 minerals, in particular patronite, descloizite, mottramite, carnotite and the titano-magnetites. Crude oil contains considerable amounts of vanadium, up to 1600 ppm, predominately in the form of porphyrin complexes [1]. Oil ash can contain up to 80 % V_2O_5. Marine organisms exhibit a wide concentration range of vanadium. High concentrations were found in sea cucumbers and molluscs [2]. The vanadium content in the shoots of most plants has no direct relationship to its concentration in the soil and is, on average, about 160 ppb for the flowering plants (with respect to their fresh weight). Concentrations between 0.4 and 80 ppm were found in freshwater aquatic plants [3]. Investigations of food showed that beverages, fats, oils, fresh fruit and vegetables contain the least vanadium (< 1 to 5 ppb), while the vanadium content of cereals, meat and milk products is 5–30 ppb and pre-prepared foods contain 11–93 ppb. In contrast, black pepper contains about 1 ppm vanadium [4, 5].

The most important technical use of vanadium is in the manufacture of various special kinds of extremely hard steel, so-called tool steel and high-speed steels. V_2O_5 is used as a catalyst in diverse oxidation processes in the chemical industry (e.g. synthesis of sulfuric acid, phthalic acid, cyclohexane, etc.). Vanadium is also utilized to manufacture glass which absorbs UV light.

Vanadium is an essential element for poultry, rats and various plants. Despite recent studies, its physiological role for humans remains largely unknown [6]. Different authors have reported that the normal daily intake of vanadium is between 12 and 28 µg/d [7] or 10 and 100 µg/d [8]. The total vanadium content of the body is 0.1–0.2 mg [6]. Investigations with ^{48}V have shown that 77% of the vanadium in plasma is bound to transferrin [9, 10]. For many years VO^{3-} has been known as a potent inhibitor of the Na^+ and K^+ ATPase (sodium pump), a common enzyme in the eukaryotic system [6, 7, 11]. Vanadium compounds can selectively increase the K^+ permeability of human erythrocytes [12, 13]. The effect of vanadium on the lipid metabolism, i.e. the biosynthesis of cholesterol, is not yet fully understood [14, 15]. Inhibition of cholesterol synthesis by vanadium, accompanied by a low plasma content of phospholipids and cholesterol, was

determined in humans and animals [14, 15]. Other authors report that cholesterol levels in the serum of rats were raised by higher doses of V_2O_5 [17]. This agrees with observations made on Polish workers who were engaged in repairing boilers. The cholesterol content in their serum rose from 1720 mg/L to 2010 mg/L while the SH-groups in the serum decreased [18]. The upper respiratory organs are particularly affected by occupational exposure to vanadium. Its compounds, especially V_2O_5, are strongly irritating to the eyes and respiratory pathways. Acute and chronic exposure cause conjunctivitis, inflammation of the mucous membranes in the nose, reversible irritation of the respiratory tract, bronchitis, bronchospasm and in severe cases asthma-like diseases [19]. According to *Thürauf* et al. [20] workers in a metallurgical plant who were chronically exposed to a vanadium concentration below the MAK value exhibit a mean vanadium concentration of 37.8 µg/L in their urine (control persons: 0.8 µg/L). These workers showed no obvious clinical toxic symptoms. Various workers in a V_2O_5 foundry in Australia developed asthma and their tongues showed a greenish colouration. Urinary excretion of vanadium decreases rapidly after the end of exposure [21–24]. Examination of 382 non-exposed persons showed a mean urinary vanadium excretion of 0.8 µg/L (range 0.05–1.44 µg/L) [25]. *Wennig* and *Kirsch* have published a comprehensive monograph about vanadium [26]. The concentration of vanadium is generally higher in urine than in blood. Thus exposure to vanadium can be more sensitively diagnosed by examination of urine.

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Contents

1 General principles

Vanadium is determined by adsorptive inverse voltammetry using the differential pulse polarographic mode (DPP) according to the standard addition procedure. After complete elimination of the biological matrix by wet oxidative mineralization, cupferron is added to form a complex with the vanadium in the solution (present in the form of VO^{2+} or VO^{3-}) at pH 8.5. This complex is enriched on a hanging mercury drop electrode (HMDE) for a specific short period. The voltage is then continuously changed in the cathodic direction and the current peak is recorded.

Aqueous solutions of NH_4VO_3 are added to the assay solution in increasing amounts for calibration.

2 Equipment, chemicals and solutions

2.1 Equipment

Inverse voltammetric electrolysis vessel (10 mL) with gas inlet, hanging mercury drop electrode (HMDE), platinum or glassy carbon auxiliary electrode, reference electrode (AgCl/Ag/ 3 M KCl) and magnetic stirrer

Power supply for the pre-electrolytic enrichment

Microdispenser, preferably an automatic microburette

Quartz apparatus for wet mineralization in an open system with attached air cooler (quartz tube, 50 cm long) or Kjeldahl flasks of quartz or quartz glass (contents 100 mL)

Dispensers, adjustable in the ranges 0.2–2.0 mL, 1–5 mL, 2–10 mL

10, 100, 500 and 1000 mL Volumetric flasks

Sealable polycarbonate centrifuge tubes (about 15 mL)

Water bath

Hand dispensers for various specific dosage volumes between 10 µL and 5 mL (e.g. Multipette from Eppendorf)

2.2 Chemicals

Ammonium vanadate (NH_4VO_3) or ammonium vanadate standard solution (1 g/L e.g. from Sigma)

96 % Sulfuric acid (e.g. from Baker)

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

25 % Ammonia (e.g. Suprapur from Merck)

30 % Perhydrol (e.g. Suprapur from Merck)

30 % Hydrochloric acid (e.g. Suprapur from Merck)

Nitrilotriacetic acid (Titriplex I, NTA) (e.g. from Merck)

Cupferron

Cresol red

Ultrapure water (ASTM type 1; R > 15 M Ω/cm)

Purified nitrogen (at least 99.999 %, in a steel cylinder)

2.3 Solutions

2 M Ammonia ammonium chloride buffer (pH 8.5):
First 75.5 mL 25% ammonia and then 89.6 mL 30% hydrochloric acid are added to about 200 mL ultrapure water in a 500 mL volumetric flask. The flask is filled to the mark with ultrapure water. The ammonia solution must be well cooled before and during the addition of the hydrochloric acid, as the heat of reaction can cause loss of ammonia. The pH value should be checked with a glass electrode and adjusted by adding concentrated ammonia or concentrated hydrochloric acid if necessary. The buffer can be stored in a glass bottle with a ground glass stopper for about a week.

Cresol red indicator solution:
A saturated solution of cresol red in ultrapure water at room temperature

0.5 M Nitrilotriacetic acid:
9.56 g nitrilotriacetic acid are weighed in a 100 mL volumetric flask, about 70 mL ultrapure water are added and dissolved by adding 7.5 mL 25% ammonia. The flask is filled to the mark with ultrapure water.

Because of its low reagent blank value Tritriplex I from Merck should be used if possible.

0.5 M Cupferron solution:
0.776 g cupferron are weighed in a 10 mL volumetric flask and dissolved in ultrapure water. The flask is filled to the mark with ultrapure water. This solution must be prepared daily.

1 M Nitric acid (for cleaning the glassware):
72 mL of 65 % nitric acid is pipetted into about 400 mL ultrapure water in a 1000 mL volumetric flask. After thorough mixing the flask is filled to the mark with ultrapure water.

2.4 Calibration standards

Stock solution:
0.1148 g Ammonium vanadate (NH_4VO_3), desiccated at 110 °C, are exactly weighed in a 500 mL volumetric flask and dissolved in ultrapure water. The flask is filled to the mark with ultrapure water (0.1000 g/L). Alternatively a commercially available standard solution (e.g. from Sigma) can be used.

Standard addition solution:
1 mL of the stock solution is pipetted into a 100 mL volumetric flask and filled to the mark with ultrapure water (1 mg/L). 10 µL of this solution contains 10 ng vanadium. This solution must be prepared daily.

3 Specimen collection and sample preparation

In order to prevent exogenous contamination all vessels used for specimen collection and sample preparation must first be rinsed with 1 M nitric acid, then three times with ultrapure water and dried in the air. Dust contamination must be prevented during drying, as dust can contain considerable amounts of vanadium.

Urine is collected in plastic bottles (high density polyethylene), acidified with cone, nitric acid (1 mL per 100 mL urine) and stored in the refrigerator (at about 4 °C) until it is processed. Analysis should be carried out within a week if possible. To obtain exact analytical results it is essential to ensure that the urine specimen is homogeneous. If any sediment has formed the urine must be vigorously shaken and warmed to 37 °C to dissolve or to homogeneously disperse the solid particles.

10 mL Urine are pipetted into the mineralization vessel (contents 100 mL) and 1 mL 65% nitric acid as well as 0.1 mL 96% sulfuric acid are added using dispensers. After the cooler has been fitted onto the apparatus it is initially heated to about 95 °C for 30 min. Then the mixture is evaporated (for about 45 min) to about 3 mL under partial reflux i.e. the gaseous or volatile substances (e.g. H_2O) are distilled off, but the unused acid condenses and flows back. At this point a spontaneous oxidation of the matrix begins.

The heat should be regulated so that this reaction is just maintained (for about 20 min) without distilling off the unused oxidizing agent (nitric acid). When the reaction is complete, evaporation of the liquid is continued until white fumes appear. However, no more heat should be supplied if the liquid begins to turn reddish-brown. In this case it is necessary to wait until the solution becomes colourless or pale yellow again. It is essential to avoid overheating and burning of the residue. The remaining colourless solution is evaporated as completely as possible with simultaneous formation of white fumes (at least 15 min). The residue is taken up with 3 mL ultrapure water and evaporated as completely as possible (intense production of white fumes). This step is repeated once. The residue is allowed to cool, 3 mL ultra-pure water and 1 mL of 30 % perhydrol are added and the solution is heated to about 100 °C for 15 min to distil off the liquid. After cooling, 3 mL ultrapure water and 2 mL of 25 % ammonia are added, and the liquid is evaporated almost to dryness. The residue is dissolved in a little ultrapure water, transferred to a 10 mL volumetric flask, which is then filled to the mark with ultrapure water. It is essential to carry out mineralization with great care to ensure the success of the inverse voltammetric determination.

Each analytical series should include two reagent blanks, in which ultrapure water is used instead of urine.

4 Operational parameters for absorptive inverse voltammetry (DPP)

The following operational parameters are intended only as a guide. Settings must be optimally adjusted for the equipment used.

Nitrogen purge time:	300 s (to drive out the gases in the assay solution)
Drop size of the Kemula electrode (HMDE):	4 notches (or position 3 for the VA-Stand 663)
Pre-electrolysis potential:	– 0.4 V (with respect to Ag/AgCl/ 3M KCl)
Pre-electrolysis duration:	10 s with stirring 10 s without stirring
Scan speed:	–10 mV/s
Trigger:	0.4 s
Voltage range (sweep):	– 0.55 V
Amplitude:	– 50 mV
Sensitivity:	e.g. 250 nA full range

5 Analytical determination

4 mL of the analytical solution are pipetted into a sealable polycarbonate centrifuge tube (about 15 mL). Then 1 mL 0.5 M cupferron solution, 200 µL 0.5 M nitrilotri-acetic acid and 4 mL buffer (pH 8.5) are added. The pH of the mixture must be 8.5. This can be checked by adding 20 µL of the cresol red solution (changes from yellow to pink). If the assay solution is too acidic the pH is adjusted by adding 25 % ammonia. The sealed vessel is warmed up to 50 °C in the water bath for 5 min. After cooling to room temperature, the solution is transferred with a little ultrapure water into the voltammetric cell. The voltammetric measurement must be carried out within 15 minutes of mixing the analytical solution with the reagents. The analytical sample is assayed under the inverse voltammetric conditions described above. The current-voltage curve is recorded between – 0.4 and – 0.95 V. The cathodic current signal produced by vanadium has its maximum at – 0.75 V. The measurement is repeated once to check the result. The reagent blank value must be determined in the same manner. If the linear range is exceeded when standards are added, a smaller aliquot of the assay solution should be taken and the voltammetric determination should be carried out anew (cf. Section 7).

6 Calibration

Calibration is carried out by adding three aliquots of the standard solution to the original assay sample and repeating the voltammetric determination in each case. After each standard addition the solution is purged with nitrogen for 10 sec.

Each addition is equivalent to a concentration increment of 2.5 µg/L expressed in terms of the urine volume assayed. Automatic dispensers have proved especially suitable for the addition of standards.

The standard additions have been chosen to give a mean vanadium concentration of 5 µg per litre urine. It has proved advantageous to select the concentrations so that after the second addition the signal is approximately twice that produced by the original sample.

7 Calculation of the analytical result

It is advisable to determine the vanadium content of the assay solution graphically from the height of the current peaks. The height of the current peak is calculated from the lowest point on the current voltage curve before it rises to its peak. A line parallel to the abscissa is drawn through the lowest point. A perpendicular is drawn from the highest point of the current peak to this parallel. This perpendicular represents the height of the

relevant current peak (cf. Figs. 1a and 1b). To obtain the calibration curve the mass of the added vanadium in ng is plotted on the abscissa and the height of the corresponding current peak (e.g. in mm) on the ordinate. The peak height value for the unspiked assay solution is inserted on the ordinate where the abscissa value is zero. A straight line is fitted through the points obtained. The vanadium mass (in ng) contained in the assay solution is given as the point where this line intercepts the abscissa. The resulting masses are divided by the urine volume in mL to give the vanadium concentration in the urine sample. The deviations of the individual results from the straight line are indicative of the quality of the analysis. Erroneous values can be readily recognized.

Assuming that only a limited number (3–5) of mineralizations are carried out simultaneously, a reagent blank must be included in every series. If only a small series is mineralized, then two reagent blank values must be included. If several series are analysed on the same day the blank value is best determined from different series. Two voltammetric determinations can be carried out from each mineralization reagent blank solution.

The evaluation can also be carried out by calculation of the linear regression. In this case, however, the results should be plotted graphically as well. The correlation coefficient does *not* give adequate confirmation of the quality of the determination.

The linear range between concentration and height of the signal is very limited for the adsorptive inverse voltammetric procedure. If the increase in current expected from the addition of the standard solution shows a continuous decline this indicates that the electrode surface is over-saturated with adsorbate (cf. Section 5).

8 Standardization and quality control

Quality control of the analytical results is carried out as stipulated in TRgA 410 of the German Arbeitsstoffverordnung (Regulation 410 of the German Code on Hazardous Working Materials) [27] and in the Special Preliminary Remarks in that volume. If standard material for quality control is not commercially available it must be prepared in the laboratory.

9 Reliability of the method

9.1 Precision

In order to determine the within-series imprecision, urine from an unexposed person which contained no vanadium was spiked with NH4VO3 and analysed 12 times. The relative standard deviation was 6.4%, which is equivalent to a prognostic range of 14.0% for a mean vanadium concentration of 2.5 µg/L.

The urine of an unexposed person containing no measurable vanadium, was spiked with 5.0 µg/L and used to evaluate the between-day imprecision. The samples were analysed on 5 different days. The relative standard deviation was 3.9%, the corresponding prognostic range was 10.7 %.

9.2 Accuracy

As no investigation material containing a known amount of vanadium was available, the urine of an unexposed person containing no detectable concentration of vanadium was spiked with a specific amount of vanadium (5.0 µg/L), then it was processed and analysed as described above. The recovery rate was 98%.

In addition, the accuracy of the method was checked by comparing it with two other methods, electrothermal atomic absorption spectrometry and inductive coupled plasma (ICP) atomic emission spectrometry. Each step in these procedures is independent of those in the method described here. Twelve urine samples were analysed in parallel (Table 1). There is a significant linear correlation between the values obtained by ETAAS (X) and those from inverse voltammetry (Y) ($Y = 0.95\ X + 0.31$; $r = 0.992$; cf. Fig. 2a). The values obtained by ICP (X) and inverse voltammetry (Y) also show a significant linear correlation ($Y = 0.96\ X - 1.24$; $r = 0.967$; cf. Fig. 2b).

9.3 Detection limit

Under the given analytical conditions the detection limit is 0.2 µg per litre urine (three times the standard deviation of the reagent blank value). The detection limit is largely dependent on the reagent blank value and the sample quantity used.

9.4 Sources of error

Serious errors can occur during the adsorptive enrichment (cf. Section 10). Not only the vanadium complex of interest in this analysis, but also any surface active substances present in the sample solution are adsorbed on the surface of the mercury drop. These

substances can inhibit or even completely prevent the adsorption of the vanadium complex. Thus it is essential to ensure that complete mineralization of all organic components of the matrix is achieved during processing of the sample.

As the adsorption can only occur on the electrode surface and only the species in the inner adsorption layer can be determined in the subsequent electrolytic reduction, the range of linear relationship between the vanadium concentration and the strength of the signal is limited and depends on the surface area of the mercury drop.

Furthermore, it should be noted that partial adsorption occurs even before current is applied to the electrode. Therefore the period between the formation of the drop and the beginning of the pre-electrolytic enrichment must be exactly defined and kept constant in each case. Thus the best results are achieved with automatically controlled devices.

An additional source of interference arises from the properties of the complex used. Its primary formation requires a period of induction. Thus a certain period of time must elapse after addition of the reagents. Thereafter the determination must be rapidly carried out, as the complex can be adsorbed on the vessel walls and the magnetic stirrer as well as on the electrode surface. Adsorption sites on the vessels can be saturated by increasing the salt concentration.

All voltammetric determination methods are highly dependent on the total electrolyte concentration in the measurement vessel. It influences the sensitivity, selectivity, but especially the course of the residual current which forms the base line of the voltammogram. The evaluation is considerably improved by addition of a compensatory buffer of high ionic strength. In the author's experience good results are obtained with 0.1 M KCl solution, as it creates conditions for the determination of the reagent blank value similar to those for the analysis. This step is advisable for all methods in which there is a great difference in the ionic strength between the blank value and the analysis, e.g. for urine. It is particularly important for all methods in which enrichment is achieved by adsorption.

Interference can also be caused by previously oxidized cupferron. A large pre-peak which appears at about –0.6 V indicates the presence of oxidized unusable cupferron. It is important to ensure that fresh cupferron is used. The substance must be white, a yellowish discolouration indicates that oxidation has already occurred. Unsuitable nitrilotriacetic acid can also lead to heightened reagent blank values. In the author's experience Titriplex 1 from Merck is most suitable for the determination of vanadium. If the reagent blank value considerably exceeds 1 µg/L, then the quality of the cupferron and Titriplex should first be checked.

It is absolutely essential to keep the pH value at 8.5 in order to achieve an exact inverse voltammetric determination of vanadium, as the formation of the vanadium cupferron complex is dependent on the pH. The complex is neither protonated nor deprotonated at pH 8.5, i.e. it is present in its uncharged form, which facilitates its adsorption on the working electrode. Therefore great care should be taken to keep the proton activity constant.

The ammonia-ammonium chloride buffer should be stored in a glass bottle with a ground glass stopper, as the volatile ammonia can escape from plastic vessels.

There is a considerable risk of contamination of the analytical sample from the reagents and vessels used, but particularly from the ambient air. It is essential to work with reagents of the highest purity. Contact with the air in the laboratory should be kept to a minimum. The vessels used must be cleaned thoroughly and stored in a dust-free environment. A check for possible contamination is absolutely necessary. If urine samples with a relatively high vanadium concentration have been analysed, the vessels used must be carefully cleaned to prevent vanadium being carried over to subsequent analyses.

The urine samples can only be stored for a limited period. They should not be kept for more than a week in the refrigerator. Vanadium determination of older urine samples can give erroneously low results.

10 Discussion of the method

Polarographic determination of vanadium on the hanging mercury drop electrode cannot be carried out in the lower µg range which is of interest in this case. It must first be enriched on a stationary electrode (HMDE). The normal inverse voltammetric technique of reduction to the element and subsequent measurement of the anodic stripping potential is only applicable for those metals which form amalgams. Vanadium does not form an amalgam. Therefore it must be converted into a suitable stable complex before the actual determination is carried out. This complex is then enriched by adsorption on the electrode surface during the so-called pre-electrolysis. In order to form the complex, the vanadium in the solution must first be converted to its highest oxidation state (+V), which is best achieved by wet mineralization as described above.

Of the various ligands tested cupferron proved to be especially suitable. The adsorbable complex contains vanadium in oxidation state +IV. Cupferron itself reduces vanadium (+V) to vanadium (+IV). In the subsequent measurement the vanadium from the complex is reduced to oxidation state +III, i.e. the potential of the working electrode is changed in the cathodic direction (–) and the resulting reduction current provides the signal for evaluation. Cupferron can form complexes with various metal ions. Such complexes can be adsorbed on the working electrode and also produce signals. Although these signals do not appear at the same voltage as vanadium and thus have no effect on the specificity of the determination, the sensitivity of the determination is greatly reduced by competitive adsorption of these species on the electrode surface. These metal ions must be masked using a ligand which acts as a strong com-plexing agent for them, but which either does not react or forms only very weak complexes with VO^{2+}. Of the many ligands which were tested the best results were obtained with nitrilotriacetic acid

(NTA). Under the selected conditions the ions which cause interference are present as stable anions and do not form adsorbable complexes, while vanadium forms the desired complex with cupferron.

The method described here permits determination of vanadium in the ecological concentration range as well as the range relevant to occupational medicine. Adsorptive inverse voltammetry is currently the most sensitive method of determination for vanadium. The limitations of this method are described in detail in Section 9.4.

As with all voltammetric methods, successful determination requires extreme care and a good knowledge of the method. An inexperienced technical assistant will probably not be able to carry it out successfully.

The current voltage curve to determine vanadium can be recorded without the differential pulse mode, but the sensitivity is considerably lower.

Members of the Working Group found that the reagent blank value can fluctuate between 0.5 and a maximum of 1.5 µg/L. A reduction, e.g. below 0.8 µg/L, can be achieved by careful selection and purification of the reagents as well as addition of a compensatory buffer of high ionic strength (cf. Section 9.4). In order to achieve a further reduction (below 0.5 µg/L) it would probably be necessary to work on a clean-bench.

Two reagent blank values should be measured in each analytical series. The mean value of both blank values is subtracted from the result for each individual sample. However, for the concentration range relevant to occupational medicine it is sufficient to analyse only one reagent blank value.

Experience has shown that the most accurate results are achieved when evaluation of the voltage curves is carried out as described in Section 7.

Mineralization of the biological matrix enables the detection of the total vanadium content in the urine, regardless of its chemical bond. Mineralization must be absolutely complete, otherwise considerable errors can occur. The specificity of the method is not only based on the formation of the complex, but also on the characteristic reduction potential of the vanadium complex. For calibration the standard solution must be prepared with vanadium(V), as it is not affected by mineralization.

In spite of the necessity for mineralization of the sample, good accuracy and sensitivity can be achieved when all the required precautions are observed. The relatively time-consuming processing of the samples limits the number of samples which can be analysed. However, the time and effort required can be considerably reduced by using automated equipment for sample processing.

In contrast to the inverse voltammetric determination of elements which form amalgams, no other metal ions in the sample can be simultaneously detected with this method. The course of the current voltage curve provides additional information on the quality of the sample processing.

Instruments used:
Differential pulse polarograph E 506, polarography stand VA 663, VA controller E 608 from Metrohm; quartz apparatus Büchi 455 from Büchi Laboratoriumtechnik

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Table 1: Comparison of the results obtained by ETAAS, ICP and inverse voltammetry.

Sample number	Vanadium concentration [µg/L]				
	ETAAS		ICP		Inverse voltammetry
1	6.2	6.1	7.6	7.4	6.2
2	9.4	9.5	12.1	12.1	9.2
3	4.0	3.7	5.0	5.0	3.9
4	22.2	20.5	23.1	13.4	19.9
5	7.0	8.6	7.8	7.1	8.5
6	11.2	9.4	12.8	13.2	10.6
7	16.7	17.7	17.5	17.6	17.9
8	2.0	–	–	–	–
9	2.0	2.0	5.0	5.0	0.8
10	14.6	13.5	15.1	15.1	12.9
11	4.8	4.8	5.6	6.1	5.3
12	2.0	2.6	5.0	5.0	3.0

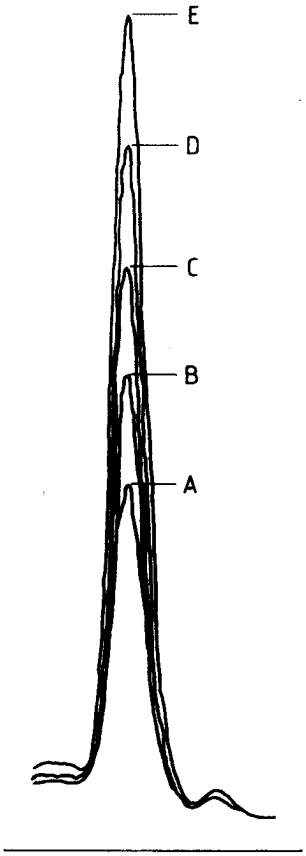

Fig. 1a: Adsorptive voltammetric determination of vanadium in urine.
A = analytical sample
B = analytical sample + 2.5 ng V
C = analytical sample + 5.0 ng V
D = analytical sample + 7.5 ng V
E = analytical sample + 10.0 ng V

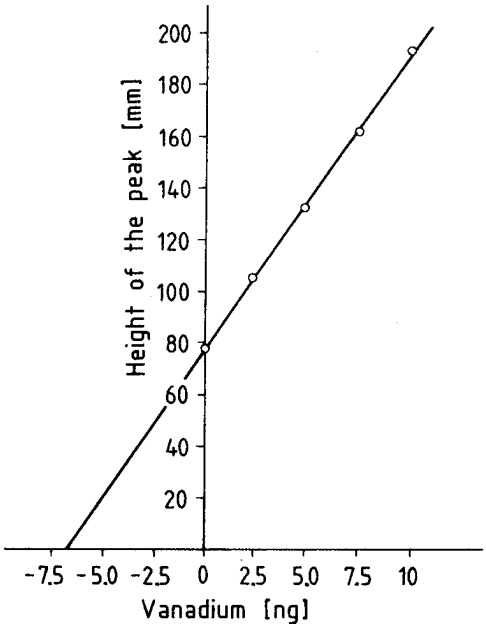

Fig. 1b: Example of a calibration curve measured using the standard addition procedure.

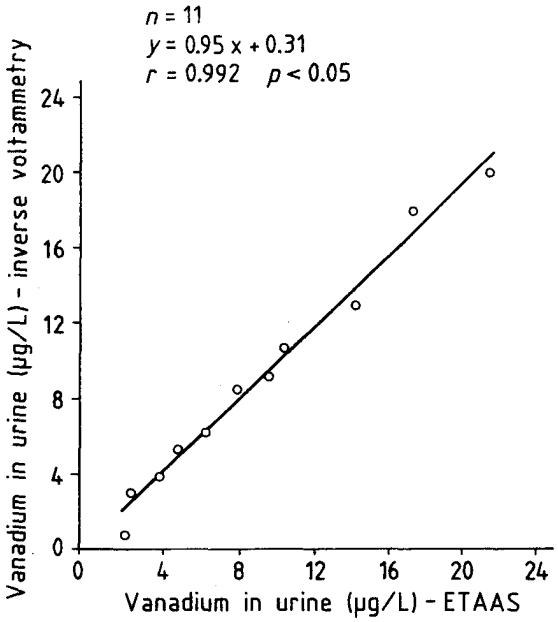

Fig. 2a: Correlation curve for the parallel analysis of 11 urine samples using inverse voltammetry and ETAAS.

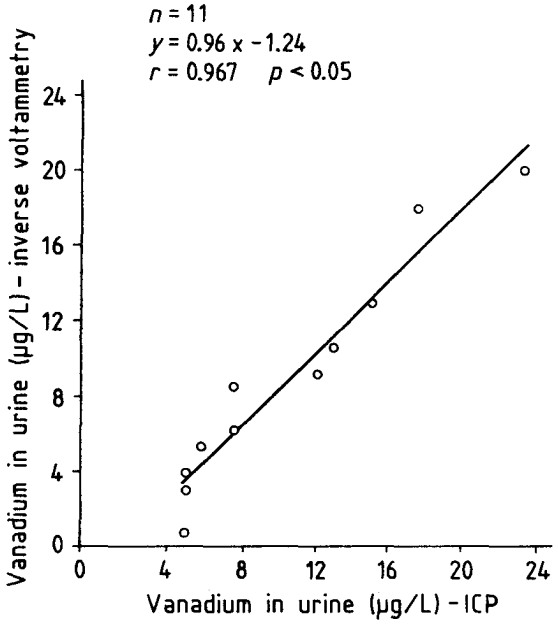

Fig. 2b: Correlation curve for the parallel analysis of 11 urine samples using inverse voltammetry and ICR