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## The electrochemical determination of ammonium based on the selective inhibition of the low-spin iron(II)/(III) system of Prussian blue

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**Abstract** A new method is described for the determination of ammonium in aqueous solutions with electrodes modified by Prussian blue (PB). The specific voltammetric response of PB-modified electrodes to ammonium ions is used for their analytical determination. In the presence of ammonium ions, a concentration-dependent inhibition of the low-spin iron(II/III) system of PB occurs. Only thallium and rubidium ions cause similar inhibition. A useful electrochemical determination method is thus available for detecting ammonium ions in the presence of frequently interfering potassium and sodium ions. Paraffin-impregnated graphite electrodes modified with a mechanically transferred PB layer and bulk-modified PB-composite electrodes are studied. The method is applicable within a concentration range which extends from  $4 \times 10^{-5}$  mol/l to  $10^{-2}$  mol/l  $\text{NH}_4^+$ . The composite electrode is used in an electrochemical flow-through system in conjunction with the Kjeldahl method.

**Key words** Prussian blue · Ammonium · Voltammetry · Flow-through · Kjeldahl

### Introduction

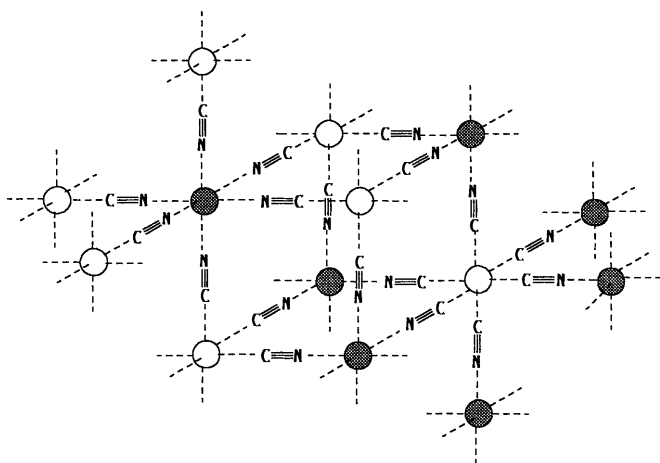
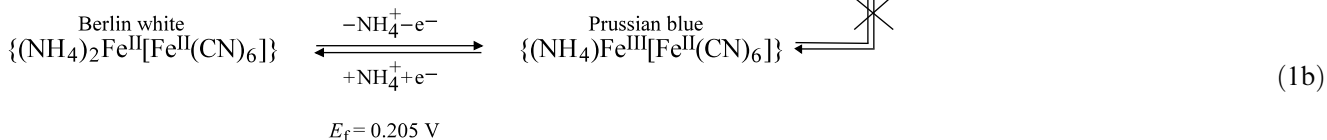
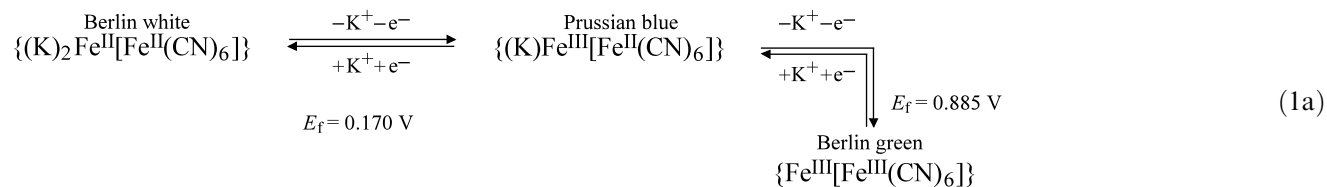
Prussian blue (PB), or iron(III) hexacyanoferrate(II), is the prototype transition metal hexacyanometalate and therefore also the most extensively studied example of this class of insoluble inorganic polymers [1–3]. Since the first cyclic voltammetric studies of PB films by Neff and co-workers [4], numerous other reports concerning

the catalytic [5–7], electrochromic [8], and voltammetric [9–13] behavior or its usage in fuel cells and batteries [14–15] or as an ion-sensitive material [16–17] have enriched our knowledge of the electrochemistry of this compound.

Figure 1 depicts a part of the cubic crystal structure of PB ( $a_0 = 10.2$  Å) with alternately arranged iron(II) and iron(III) ions and linear cyanide bridges. In this way, iron(II) ions are surrounded by the carbon sides of the cyanide ions, and iron(III) ions are linked by the nitrogen ends of the cyanides, which results in a low-spin and a high-spin electron configuration, respectively. If PB is cyclically polarized in contact with an electrolyte solution containing a suitable alkali ion supporting electrolyte, two different stable peak systems can be observed (Fig. 3). They are caused by the redox reactions of the iron(III) and iron(II) ions (Eq. 1a).

The zeolitic structure of PB allows a concerted electron and ion diffusion by which the necessary charge balance is maintained. The situation is different with selected group I, II, or transition metal ions. In an earlier publication we have shown that cadmium ions are able to enter not only the interstitial positions but can also substitute the regular-sited nitrogen-coordinated metal ions, i.e. the high-spin iron of PB, in an electrochemical driven reaction to form solid cadmium hexacyanoferrate [10]. Following this idea, we have recently described other hexacyanoferrates which are accessible to such an insertion/substitution reaction, i.e. silver(I) hexacyanoferrate with cadmium ions and PB with nickel ions [20]. In this way we prepared bilayered structures of these hexacyanoferrates, which were studied using cyclic voltammetric and chronocoulometric methods. Another paper features the size-specific voltammetric behavior of solid PB in contact with thallium- or rubidium-containing solutions, i.e. the inhibition of the low-spin iron system, which can be explained in terms of a geometric model of the three redox states of PB [18]. As shown in a recent paper, thallium ions can be enriched from the adjacent bulk solution

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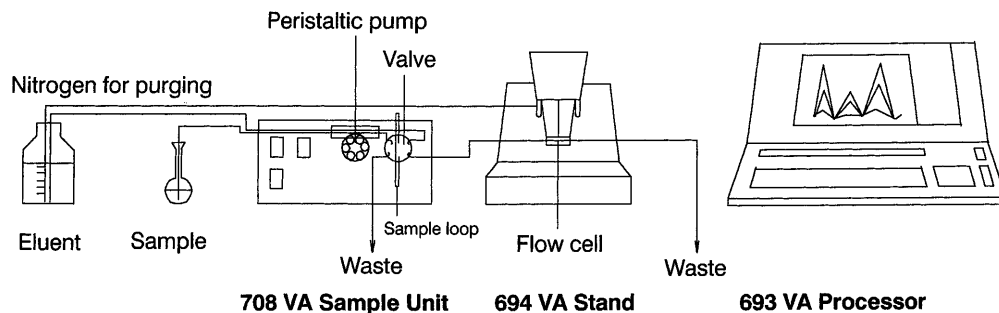


**Fig. 1** The lattice of Prussian blue. The *dark* and *light* balls symbolize high-spin and low-spin iron centers, respectively. Interstitial ions are not shown

and determined following the inverse voltammetric thallium response [19].

In this paper a different method was chosen, since a similar determination step is not possible for ammonium. Therefore, the indirect proportionality between the analyte concentration and the low-spin iron peak was used for the ammonium determination.

**Fig. 2** The first 8 cyclic voltammograms of Prussian blue, immobilized on the surface of a PIGE. Electrolyte solution 0.1 M  $KNO_3$ , scan rate 0.5 V/s, start potential  $-0.2$  vs Ag/AgCl



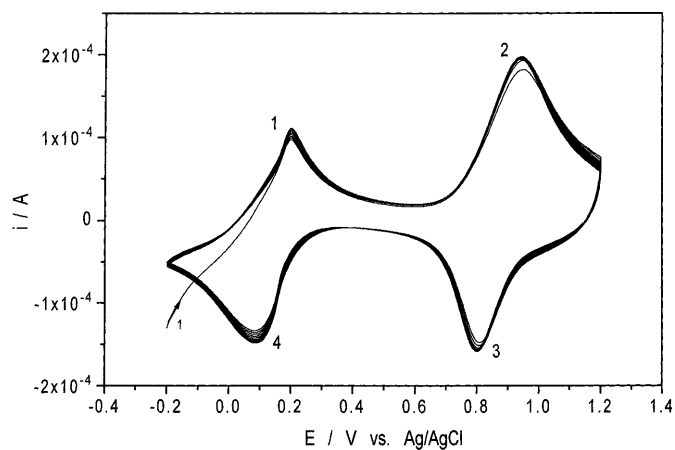
## Experimental

### Equipment

1. Voltammetric batch experiments were carried out with an Autolab/PGSTAT 20 potentiostat (Eco-Chemie, Utrecht/Netherlands) equipped with a VA 663 electrode stand (Metrohm, Herisau/Switzerland) and an 80386 personal computer. The GPES 3 software (Eco-Chemie) was used. An Ag/AgCl electrode filled with 3 M KCl ( $E = 0.208$  V vs SHE,  $T = 298$  K) and a glassy carbon rod served as reference and auxiliary electrodes, respectively. The working electrodes are described below.
2. The novel, fully automatic Electrochemical Flow-through Trace Analyzing system "EFTA" (Metrohm, Herisau/Switzerland) as shown in Fig. 2 was used for the voltammetric application of the PB-composite electrode in flow-through systems. The electrochemical flow-through cell operates in the three-electrode configuration with an Ag/AgCl (3 M KCl) reference electrode ( $E = 0.208$  V vs SHE), a glassy carbon auxiliary electrode and a solid-state composite electrode with a geometrical surface of  $2.3 \text{ mm}^2$  exposed to the flowing solution. Two different solutions can be introduced into the flow system by a peristaltic pump system. The solution passes the working electrode at a rate of  $1.5 \text{ ml/min}$ . The control of both the flow-through system and the electrochemical measurements as well as the data handling were performed with the VA 693 processor.

### Electrodes

1. Paraffin-impregnated graphite electrodes (PIGEs) with a circular surface diameter of  $5 \text{ mm}$  were used to perform voltammetric experiments with microcrystalline PB. The pre-



**Fig. 3** Block diagram of the automated electrochemical flow-through trace analyzing system EFTA (Metrohm)

paration of the impregnated graphite rods as well as the immobilization of the solid PB particles on the electrode surface have been described elsewhere [22, 23].

- For the preparation of the solid PB bulk-modified composite electrodes, PB (20 wt%), graphite (60 wt%) and paraffin (20 wt%) were intimately mixed. First the graphite and PB were mixed for 10 min in a ball mill; then the paraffin was added and the mixing was continued for another 5 min. The final product was slowly heated in a water bath until the paraffin was melted, then filled into a cylindrical mold of a mechanical spindle press and pressed into rods with a diameter of 5 mm and a length of 40 mm. The electrode rod was additionally coated with a thin layer of melted paraffin, except for the lower circular surface and the upper end.
- The composite electrode for use in the EFTA unit was of the following composition: 5 wt% PB, 90 wt% graphite, and 5 wt% paraffin. The solid mixture was prepared as described above. Small amounts of it were gently pressed into a cylindrical hole of the electrode plate of the flow-through cell and smoothed with a PTFE spatula.

## Reagents

$\text{H}_2\text{SO}_4$  (Merck, Darmstadt/FRG),  $\text{KNO}_3$ , and  $\text{NaNO}_3$  (VEB Laborchemie Apolda/former GDR) electrolyte solutions were prepared from analytical grade reagents. A Merck commercial standard of  $\text{NH}_4\text{Cl}$  (1000 mg/l) was diluted for the calibration measurements. The electrodes were prepared with graphite powder, spectroscopic grade (VEB Germed, Dresden/former GDR) and paraffin powder with a m.p. of 56°–58 °C (VEB Germed, Dresden/former GDR).

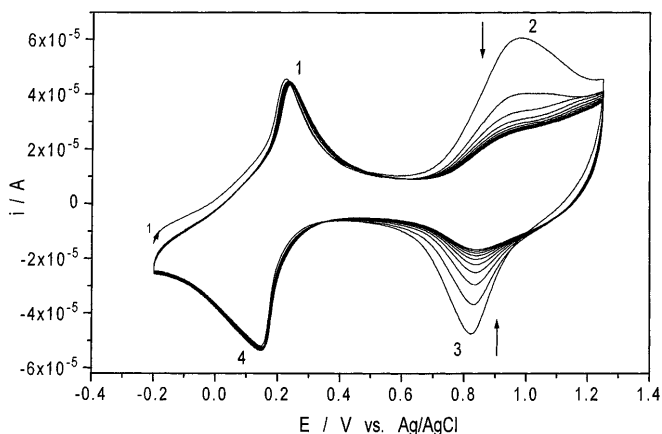
PB was prepared according to the following procedure: 4.73 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 200 ml 0.1 M HCl and added dropwise to a well-stirred solution of 7.36 g  $\text{K}_4\text{Fe}(\text{CN})_6$  in 100 ml water. After addition, the mixture was stirred for a further 15 min. The dark-blue precipitate was filtered off, washed with some portions of distilled water and dried for several days in an evacuated desiccator at ambient temperature. The substance was analyzed with respect to its contents of K, Fe (using atomic absorption spectroscopy), C, H, and N. The following data were obtained, suggesting a general formula of  $\text{KFe}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ : K 9.28, Fe 30.68, C 17.69, H 2.55, N 20.14. For all measurements, twice-distilled deionized water was used.

## Results and discussion

### Effect of ammonium on the voltammetric Prussian blue response

Figure 4 depicts repetitive cyclic voltammograms of a PB-modified electrode in contact with an aqueous electrolyte solution containing 0.1 M  $\text{KNO}_3$  and 0.05 M  $\text{NH}_4\text{NO}_3$ . The PB was mechanically immobilized on the surface of a PIGE. As in the case of a pure 0.1 M  $\text{KNO}_3$  electrolyte solution (Fig. 3) there are two well-defined voltammetric systems, which can be assigned to the one-electron redox processes of the high-spin iron (peaks 1 and 4) and the low-spin iron centers (peaks 2 and 3), respectively (Eq. 1b). During the repeated cyclic polarization, the low-spin system is rapidly decreasing. The formal potential  $E_f = 1/2(E_p^a + E_p^c)$  of the high-spin iron system,  $E_p^a$  and  $E_p^c$  being the anodic and cathodic peak potentials of the considered system, respectively, shifts by 55 mV versus  $\log a_{\text{K}^+}$  and 55 mV versus  $\log a_{\text{NH}_4^+}$ , which reflects the reversible exchange of potassium and ammonium ions for these electrochemical reactions. The high-spin redox reaction under participation of ammonium has to be formulated as in Eq. 1b. The deactivation of the low-spin redox system is due to small changes in the structure of the hexacyanoferrate taking place upon redox cycling. The values of the lattice constants and the radii of ionic channels and interstitial sites of Berlin white (BW), Prussian blue (PB) and Berlin green (BG) are summarized in Table 1.

Very recently, it has been demonstrated that thallium and rubidium are of such a size that although they are able to diffuse in the crystal lattice of BW, they cannot diffuse in the PB lattice. The same is true for the hydrated ammonium ions, which have a radius of 175 pm [21] (For the sake of comparison: the radius of potassium is 165 pm [21]). The “breathing” of the crystal



**Fig. 4** The first ten cyclic voltammograms of Prussian blue, immobilized on the surface of a PIGE. Electrolyte solution 0.1 M  $\text{KNO}_3$ , 0.05 M  $\text{NH}_4\text{NO}_3$ , scan rate 0.05 V/s, start potential  $-0.2$  V vs Ag/AgCl

**Table 1** Lattice parameters of Berlin white, Prussian blue and Berlin green

	Lattice constant $a_0$ [Å]	Radius $r_c$ of ionic channels [pm]	Radius $r_i$ of interstitial sites [pm]
Berlin white	10.43	83.7	191.7
Prussian blue	10.16	77	192
Berlin green	10.39	82.7	190

lattice during redox switching leads to the characteristic voltammetric behavior described. Since the ammonium diffusion can occur in the widened structure of BW, there are no restrictions for the oxidation from BW to PB and its re-reduction under expulsion or uptake of one ammonium ion. The first oxidation step is accompanied by a lattice contraction, and the second ammonium ion cannot diffuse through the solid PB matrix. These interstitial ions are practically stuck in the lattice structure, so that a further oxidation to BG is prevented because the necessary charge neutrality of the solid cannot be achieved. This is the reason why the electrochemical response disappears during repetitive potential cycles.

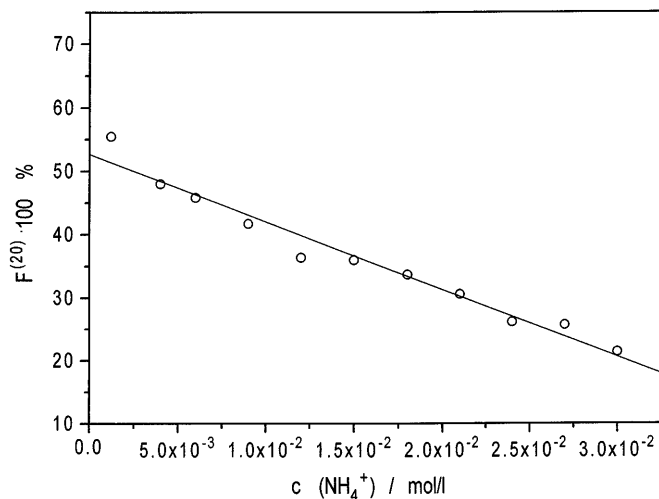
## Analytical Applications

### Determination of ammonium by voltammetry

The disappearance of the low-spin iron system of PB in the presence of ammonium ions can be used for the analytical determination of ammonium ions in aqueous solutions. First attempts were made using the voltammetry of microcrystals of PB. Before each measurement, small amounts of solid PB were mechanically immobilized on the surface of a paraffin-impregnated graphite electrode. After this procedure, the electrode was placed in 0.1 M KNO<sub>3</sub> and the potential was cyclically scanned with 100 mV/s between -0.3 and 1.3 V until reproducible and stable voltammograms of PB appeared (Fig. 2). Then the electrode was carefully washed with water and transferred to the measurement cell containing a known concentration of ammonium standard solution in 0.1 M KNO<sub>3</sub>. In the stirred solution, a number of cyclic voltammograms (20, for example) were recorded. Taking the cathodic peak current  $i_{p3}^{(1)}$  of the low-spin iron system in the first cycle as the reference value, it is possible to calculate the following value from the twentieth cycle:  $\frac{i_{p3}^{(20)}}{i_{p3}^{(1)}} = F^{(20)} \cdot F^{(20)}$  depends almost linearly on the ammonium concentration (Fig. 5). The experimental points are the average of 5–7 replicate determinations. A typical relative standard deviation at  $c(\text{NH}_4^+) = 0.004$  M was 0.86% ( $n = 7$ ).

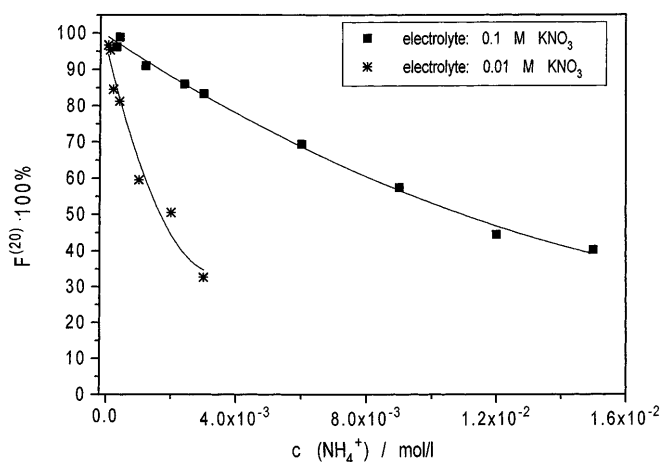
### The use of reactrodes

Further measurements were performed using PB-based bulk-modified reactive composite electrodes, or so-



**Fig. 5** Dependence of  $F^{(20)}$  on the concentration of an  $\text{NH}_4\text{NO}_3$  solution for a PB-modified PIGE. All data were collected in a 0.1 M KNO<sub>3</sub> supporting electrolyte

called *reactrodes*. These electrodes generally have a better long-term stability of the electrochemical response, although the obtained peak systems are usually less reversible than in the voltammetry of mechanically immobilized microparticles of PB. This behavior can be attributed to the content of organic binder, i.e. paraffin. For our purposes, however, the reactrodes are suitable, as  $i_{p3}$  is always easy to measure. For the sake of comparison with Fig. 5, Fig. 6 also shows calibration curves of PB reactrodes for the function  $F^{(20)}$ . Here, the calibration curve is additionally shown with a tenfold dilution of the supporting electrolyte. It is remarkable that the supporting electrolyte concentration influences the sensitivity and dynamic range of the measurements. With higher concentration, there is a wider dynamic concentration range, but the slope of the calibration



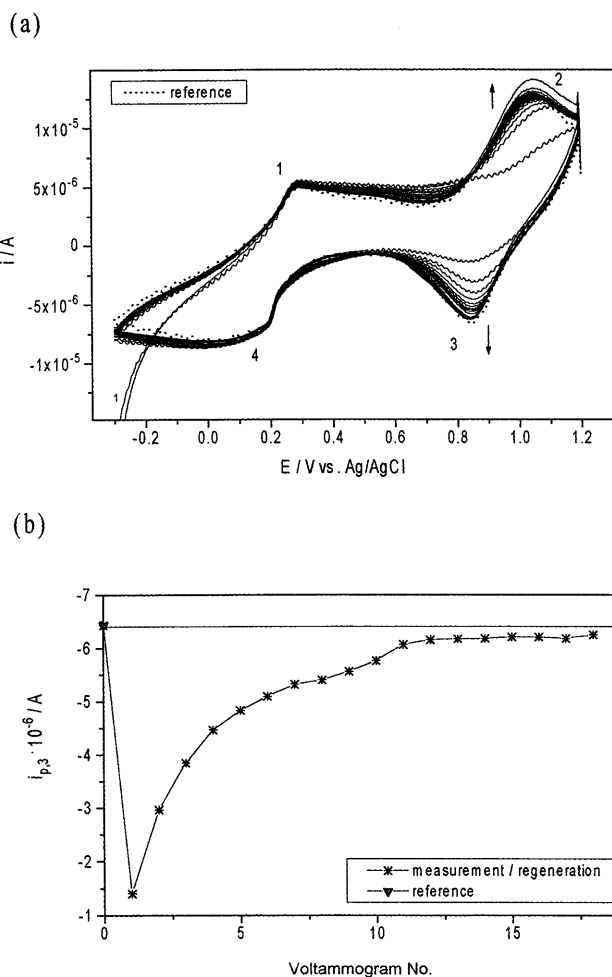
**Fig. 6** Dependence of  $F^{(20)}$  on the concentration of an  $\text{NH}_4\text{NO}_3$  solution for PB-bulk-modified reactive composite electrodes (reactrodes) using different supporting electrolytes 0.1 M KNO<sub>3</sub> (■) and 0.01 M KNO<sub>3</sub> (\*)

curve and the precision are higher for lower electrolyte concentrations. A minimum concentration of approx.  $10^{-2}$  M  $K^+$  and a relative decrease in  $i_{p3}$  of approx. 30% ( $F^{(x)} \approx 0.3$ ) are required in order to allow a quantification of the  $NH_4^+$  concentration. The peaks were also sharper in the case of a higher concentration of electrolyte. For this reason and because of the generally better responses in a potassium-containing solution (compared with other alkaline salts), a  $KNO_3$  concentration of 0.1 M (or higher) was used throughout the studies. Under these conditions while using the function  $F^{(20)}$ , a working range from  $5 \cdot 10^{-4}$  mol/l to  $2 \cdot 10^{-2}$  mol/l was readily available, despite the fact that the calibration curves were nonlinear. The standard deviations were similar to that in Fig. 5.

#### Automatic ammonium determination in a flow-through system

The determination of ammonium ions with a PB based reactrode should lend itself very well for automatization in a flow-through system. The newly developed system EFTA (Metrohm) (Fig. 3) excellently supports complex electrochemical measurements in a flow-through cell and allows free programming of the solution fluxes. When the composite electrode was made as for the batch experiments, the obtained voltammograms were highly  $iR$ -distorted. Therefore, the composition of the electrode material was changed in such a way as to reduce the paraffin content. For the use of the PB reactrode in a flow-through cell the most important prerequisite was the possibility of reactivating the low-spin iron system. This is indeed possible by cyclic polarizations in a concentrated  $KNO_3$  solution. In this case, the expulsion of ammonium ions in the solid can compete with that of potassium ions (in the oxidative half-cycle), because under these conditions the redox potential is shifted to more positive potentials.

The long-time behavior and stability of the electrode were studied. Figure 7a depicts 18 repetitive cyclic voltammograms in 1 M  $KNO_3$  following an accumulation period of five cyclic scans in a flowing solution of  $10^{-2}$  M  $NH_4NO_3$  in 0.05 M  $H_2SO_4$ . Additionally, the reference voltammogram is shown with 1 M  $KNO_3$  solution before accumulation. Figure 7b illustrates the corresponding peak currents of the reduction processes from BG to PB, i.e.  $i_{p3}$ . Only after 10–12 voltammetric scans was a stable value of 96% of the reference peak current finally obtained. The example given is representative of the complete measurement series. The constant 4% decrease based on the initial values of  $i_{p3}$  may be attributed to the influence of the constant flowing system on the electrode surface and the slight loss of electroactive species following therefrom. It should be noticed that an exhaustion can be excluded, since the same value was found for the voltammetric high-spin system, which is not involved in the ammonium-specific decrease/increase processes.



**Fig. 7a, b** Eighteen repetitive cyclic voltammograms of a PB-based composite electrode of the EFTA unit, following five accumulation cycles of ammonium. Additionally, the reference voltammogram before accumulation is shown. Electrolyte solution 1 M  $KNO_3$ , scan rate 0.03 mV/s, start potential  $-0.3$  V vs Ag/AgCl, Flow rate 1.5 ml/min. **a** Cyclic voltammetric curves. **b** Peak currents  $i_{p3}$

To simulate a practical application, dilute sulfuric acid containing the analyte was used, since this is the electrolyte typically obtained in a Kjeldahl analysis.

First and only once in each series after preparation of a new PB electrode, the latter was conditioned by potential cycling in a flowing solution of 1 M  $KNO_3$ . Before each measurement, one reference voltammogram was taken with the following parameters: begin and start potential  $-0.3$  V, end potential 1.2 V, scan rate 30 mV/s, flow rate 1.5 ml/min. After this, a sample of an ammonium ion standard solution in 0.05 M  $H_2SO_4$  was transferred through the cell while the potential was cycled for a definite number of scans with the above given CV parameters. Then another scan was recorded in a 1 M  $KNO_3$  solution to determine the degree of decrease in the peak current  $i_{p3}$ . The next step was the regeneration of the electrode in order to prepare it for the next measurement. This was also performed in 1 M  $KNO_3$ . Between two accumulation steps, there

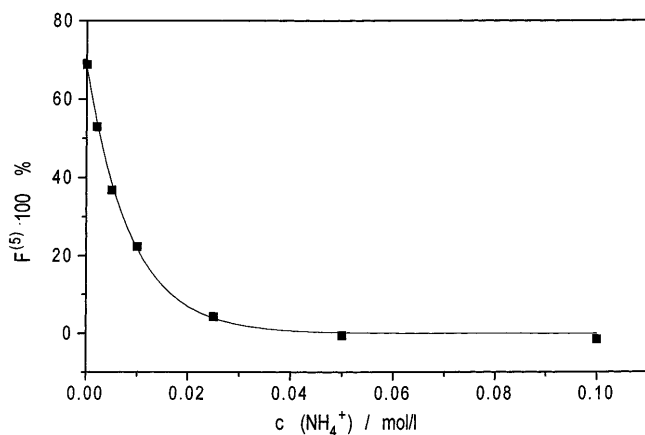


Fig. 8 Dependence of  $F^{(5)}$  on the concentration of an  $\text{NH}_4\text{NO}_3$  solution for the automatized determination with the PB flow through electrode

were altogether 14 scans under flow-through conditions with a 1 M  $\text{KNO}_3$  solution, the first of these scans being the determination of the previous measurement and the last the reference determination of the next measurement. In this way, one composite electrode could be used for more than 50 measurements. A typical calibration plot (the function  $F^{(5)}$ ) for five accumulation cycles with an ammonium-containing eluent is shown in Fig. 8. For concentrations higher than  $2 \times 10^{-2}$  M  $\text{NH}_4^+$ , the calibration line is curved.

## Conclusions

In this communication, a new method for the determination of ammonium ions is presented, following a selective size-specific inhibition process of the low-spin iron voltammetric system of solid Prussian blue (PB). For use as a voltammetric sensor, PB can be attached by mechanical deposition on the surface of a paraffin-impregnated graphite electrode or immobilized via bulk-modification in a PB *reactrode*. The surface of this *reactrode* can be regenerated after measurement.

The utilized inhibition effect is very specific, as only  $\text{Rb}^+$ ,  $\text{Tl}^+$  and  $\text{NH}_4^+$  can cause it. Also, the likely circumstances under which analyses for these elements might be required are so different that detection of more than one of them in one analysis is very unlikely. Nonspecific interferences by other solution constituents can be circumvented by using an electrolyte solution of constant composition as obtained in Kjeldahl analyses.

The composite electrode possesses sufficient mechanical and voltammetric stability for it to be used in

an automated electrochemical flow-through system. The electrochemical re-activation of the low-spin iron system after its inhibition by ammonium ions allows the use of one *reactrode* over an extended period.

An EFTA unit can be coupled with the Kjeldahl nitrogen determination method commonly used for routine determinations of organic bound nitrogen in a wide range of materials in many analytical laboratories. Especially in this case, the PB *reactrode* offers advantages for an automatic determination of ammonium ions.

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