

Note

Determination of nitrates in nickel hypophosphite for chemical nickel plating by means of high-speed analytical isotachopheresis

P. BOČEK, S. PAVELKA, M. DEML and J. JANÁK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 66228 Brno (Czechoslovakia)

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During chemical nickel plating processes, sometimes the yield relative to the nickel placed in the bath decreases or even the bath does not function. Baths that showed such behaviour contained considerable concentrations of nitrates. The interference of nitrate with the deposition of nickel from the bath is obviously analogous to its effect on the reduction of cations by metallic zinc¹. The source of nitrate anions in the bath is impurities of the basic raw materials, *i.e.*, nickel hypophosphite, which is produced by the reaction of sodium hypophosphite with nickel nitrate. The determination of nitrate, however, is difficult. The bath is prepared by the dissolution of nickel hypophosphite in a calculated amount of ammonia solution, followed by addition of lactic acid to the nickel ammine complex that is formed such that the pH of the solution is *ca.* 5.6. The bath contains both hypophosphites and phosphites. With baths that are ready for use it is therefore necessary to determine nitrates in a medium containing lactates, hypophosphites, phosphites, nickel and ammonium salts.

In the past, the nitrate content has been measured by reduction with Devarda's alloy and ammonia distillation and titration. This procedure, as well as most other indirect methods for the determination of nitrates, is laborious and the ammonium salts present interfere. Direct methods such as those using ion-selective electrodes are insufficiently selective^{2,3}.

Many workers have recently used model mixtures to demonstrate the possibilities of isotachopheresis and some of its advantages over classical methods (for a review, see ref. 4). Very few practical methods, however, have been developed so far. This paper gives an example of the rapid and simple determination of nitrates in nickel hypophosphite for chemical nickel plating by means of analytical isotachopheresis⁵.

EXPERIMENTAL

The analyses were carried out in an isotachophoreograph of the authors' own design^{5,6}. The system 0.01 *M* hydrochloric acid-0.04 *M* β -alanine (Loba-Chemie, Vienna, Austria) of pH 4.0 without other additives served as the leading electrolyte and 0.01 *M* glutamic acid was used as the terminator. The separation was carried out at a constant current of 400 μ A and 22°. The total time necessary for the analysis

was about 6 min. All of the chemicals used were of analytical-reagent grade and they and the samples of nickel hypophosphite for currentless nickel plating were obtained from Lachema (Brno, Czechoslovakia).

Several grams of each sample of nickel hypophosphite were homogenized in a mortar and approximately 2.4 g were made up to 1 l of solution. The injections of the samples and the standard solution (0.004 M sodium hypophosphite + 0.06 M sodium nitrate) were carried out with the aid of a 10- μ l Hamilton microsyringe. The analysis of each sample was repeated three times.

RESULTS AND DISCUSSION

The leading electrolyte of pH 4.0 with the leading chloride anion and buffering β -alanine counter ion was selected for the determination of nitrates in nickel hypophosphite, with glutamate as the terminating ion. The reason for this choice is the adequate differences between the effective mobilities of nitrate, hypophosphite and glutamate at this pH. In addition, the mobility of glutamate is still sufficiently great that a high current can be used for the separation and therefore the analysis can be performed quickly. This is demonstrated in Fig. 1 for the analysis of a model mixture containing nitrates, hypophosphites, phosphites, phosphates and lactates, each at a concentration of 0.004 M.

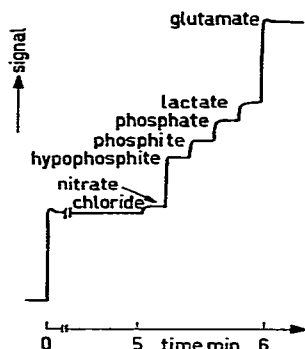


Fig. 1. Analysis of a model mixture containing nitrates, hypophosphites, phosphites, phosphates and lactates, each at a concentration of 0.004 M. Volume of mixture injected, 3 μ l. Leading electrolyte, 0.01 M HCl and 0.04 M β -alanine, pH 4.0. Terminating electrolyte, 0.01 M glutamic acid. The separation was carried out at a constant current of 400 μ A and 22 $^{\circ}$.

Under the conditions described above, the contents of nitrates in the samples of nickel hypophosphite taken from different batches varied in the range 0–14.8% of the total amount of soluble substances in the sample. Quantitative evaluation of the isotachopherograms was carried out by direct comparison of the step lengths corresponding to the nitrate concentration at a certain amount of sample injected (3 μ l) with the step length for the same volume of standard solution. The relative coefficient of variation for the determination by this procedure was about 2%.

Fig. 2 shows the results of three isotachopheretic analyses. Fig. 2a shows the analysis of a standard mixture of hypophosphite and nitrate. Fig. 2b shows the

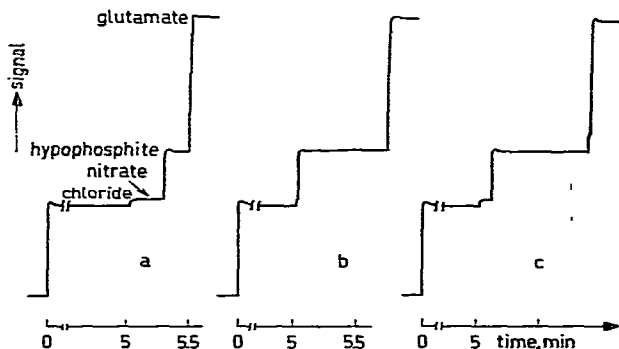


Fig. 2. Isotachophoregrams: (a) standard mixture of hypophosphite and nitrate ($0.004\text{ M NaH}_2\text{PO}_2 + 0.006\text{ M NaNO}_3$); (b) sample of nickel hypophosphite of acceptable quality (bath plating nickel well); (c) sample of nickel hypophosphite of inferior quality, containing 4.9% of nitrates (bath prepared from this sample did not function). For separation conditions, see Fig. 1.

analysis of a sample of nickel hypophosphite that was used for the preparation of a nickel plating bath that functioned well. The content of nitrates in the sample was below the detection limit of isotachophoresis with the experimental arrangement used (less than 0.2%). Fig. 2c shows the analysis of a nickel hypophosphite sample containing 4.9% of nitrates. The bath prepared from this sample did not function. The total amount of nitrogen in this sample was determined by elemental analysis for control purposes⁷ and corresponded to a nitrate content of 4.96%, which agreed well with the value of $4.9 \pm 0.1\%$ found by isotachophoresis. In addition, small amounts of phosphite produced by hypophosphite oxidation were also found in some samples.

REFERENCES

- 1 A. Okáč, *Qualitative Analytische Chemie*, Akademie Verlagsgesellschaft, Leipzig, 1960, p. 175.
- 2 J. Koryta, *Ion-Selective Membrane Electrodes*, Cambridge University Press, Cambridge, 1975.
- 3 D. Weiss, *Chem. Listy*, 69 (1975) 202.
- 4 F. M. Everaerts, J. L. Beckers and Th. P. E. M. Verheggen, *Isotachophoresis: Theory, Instrumentation and Applications*, Elsevier, Amsterdam, Oxford, New York, 1976.
- 5 P. Boček, M. Deml and J. Janák, *J. Chromatogr.*, 106 (1975) 283.
- 6 M. Deml, P. Boček and J. Janák, *J. Chromatogr.*, 109 (1975) 49.
- 7 V. Rezl and B. Kaplanová, *Microchim. Acta*, (1975) 493.