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Short Communication

Spectrophotometric Determination of Nitroprusside by Complex Formation with Obidoxime

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Summary. A method for the determination of small amounts of nitroprusside is proposed. Reaction with obidoxime leads to a coloured complex of high molar absorptivity which can be detected spectrophotometrically.

Keywords. Nitroprusside; Obidoxime; Spectrophotometry.

Spektrophotometrische Bestimmung von Nitroprussid durch Komplexbildung mit Obidoxim (Kurze Mitt.)

Zusammenfassung. Eine Methode für die Bestimmung kleiner Mengen Nitroprussid wird vorgeschlagen. Die Methode beruht auf der Reaktion des Nitroprussids mit Obidoxim unter Bildung eines farbigen Komplexes mit hoher Molarabsorption, die man spektrophotometrisch messen kann.

Nitroprusside (*NP*), sodium nitrosylpentacyanoferrate(II), is a potent hypotensive drug [1] and a well known analytical reagent which has been widely suggested for visual and spectrophotometric detection and determination of many organic and inorganic compounds. The proposed methods of analysis are mostly based on the fact that *NP* in very alkaline media or under UV light forms with series of compounds coloured complexes either of the additional or of the substitutional type. It has been used for the detection of active methylene groups [2], aldehydes [3] and methyl ketones [4], aromatic and biogenic amines [5, 6] and aminoacids [6, 7]. Moreover, spectrophotometric determinations of guanidine groups [8], hydroxylamine, aminoacids, thiosulphate, thiocyanate and thiourea ions [9], primary aminoalcohols [10], sulfides [11], sulphites and sulphur dioxide [12], heterocyclic mercaptans [13], and oximes [14–19] have been developed. Thus procedures for the determination of *NP* appear to be of interest with respect to indirect methods of determining other compounds.

Titrimetric, gravimetric, polarographic, coulometric and spectrophotometric methods have been proposed for the determination of *NP* [20]. Few procedures were described in recent times which are based on the spectrophotometric determination of the nitrites occuring from the dissociation of *NP* in alkaline solutions

Table 1. Precision of the determination of *NP* with obidoxime

μg *NP*	*A*	μg *NP* found*	Standard deviation, μg	Rel. std. devn., %	No. of detns.
7.45	0.064	7.60	0.34	4.52	9
74.50	0.476	73.03	1.66	2.27	7
148.98	0.908	141.60	2.28	1.61	5

* Calculated by means of the calibration equation: $y = 0.0063x + 0.0161$, $r = 0.9999$; x is expressed in μg/5 cm^3 of the reaction mixture

[21, 22] as well as a high performance liquid chromatographic determination [23], and a determination of *NP* by its inhibitory effect on the photolysis of the methylviologen-*EDTA*-acridine system [24]. We now present a new method for the direct spectrophotometric determination of microquantities of *NP* with obidoxime.

1,1'-Bis(pyridinium-4-aldoxime)oxydimethylene dichloride (obidoxime, LüH-6, Toxogonin®) is an organophosphorus antidote [25] which is known to form a blue coloured oximatopentacyanoferrate(II) complex with strongly alkaline solutions of *NP*. The characteristics of the complex and the optimum conditions for its formation have been described [26]. Owing to the appearance of a new strong charge-transfer band in the visible region upon complex formation ($\lambda_{max} = 615$ nm, $\varepsilon = 11000\ dm^3\ mol^{-1}\ cm^{-1}$) this reaction has been earlier successfully employed for the detection and determination of small amounts of obidoxime in pharmaceutical preparations [14] and biological materials [18, 19].

Now we applied this reaction for the spectrophotometric determination of microquantities of *NP*. The concentrations of the reactants were inverted such to let the obidoxime be at least in a 40-fold molar excess over *NP* and to ensure the independence of the absorbance value from the molar ratio of the reactants. The optimum *pH* for the reaction ($pH \geqslant 11.7$) was maintained by an adequate excess of sodium hydroxide. Beer's law was obeyed up to an absorbance of 1.0. The useful range was 7.5–156 μg of *NP*. The actual results and the linear concentration-absorbance relationship obtained by regression are presented in Table 1. Species reacting with pentacyanoferrate(II) ions under the conditions used can interfere. So did Cu^{2+}, Hg^{2+}, Au^{3+}, pyridine derivatives [27], alkyl and aryl hydrazines and hydroxylamines [28]. A 60-fold molar excess of uric acid and 150-fold molar excesses of creatinine and urea did not interfere. To utilize this reaction for the determination of *NP* in biological materials is presently studied.

All reagents used were of analytical-reagent grade. $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (*NP*) solution, 5×10^{-4} *M*, was prepared from a Kemika (Zagreb) reagent. It remained stable for a few days in the dark. More dilute solutions were obtained by appropriate dilution with water. Obidoxime, 0.02 *M*, was used in the form of Toxogonin® (Merck). Its water solution remained stable for days.

The determinations were performed according to the following procedure: To 1 cm^3 of 0.1 *M* sodium hydroxide, 1 cm^3 of the sample solution containing 7.45–148.98 μg of *NP* was added. The mixtures were shaken and kept in the dark for 10 min. 2 cm^3 of water and 1 cm^3 of the obidoxime solution were than added. After 2–3 min the absorbances were measured against water at 615 nm.

Spectrophotometric measurements were made with a UNICAM SP 600 UV spectrophotometer and 1 cm glass cells.

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