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## Precise and sensitive determination of nitrite by coulometric backtitration under flow conditions

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**Abstract** A novel method performing for coulometric backtitrations in flow channels was developed, which was applied for the precise and sensitive determination of low concentrations of nitrite. Under acid conditions nitrite is reacting stoichiometrically with hydrazine, the remained excess of which is backtitrated with electrogenerated bromine. The titration course is recorded either amperometrically or chemiluminometrically. Hydrazine can be determined precisely and accurately in the range between 0.1  $\mu\text{M}$  and 1 mM without calibration. Nitrite is reduced by hydrazine according to the reaction  $2 \text{NO}_2^- + 2 \text{H}^+ + \text{NH}_2\text{-NH}_2 \rightarrow \text{N}_2\text{O} + \text{N}_2 + 3 \text{H}_2\text{O}$ . Applying the amperometric and the chemiluminometric end-point location nitrite was determined accurately and precisely in the ranges 0.25–65  $\mu\text{M}$  and 0.10–50  $\mu\text{M}$ , respectively. The method was applied to the determination of nitrite in tap and river water.

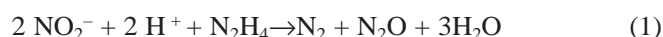
### Introduction

Nitrite is a common and toxic pollutant found in many natural and artificial water reservoirs [1, 2]. Besides, after the absorption of  $\text{NO}_x$  in water nitrite is formed as a side product of microbial nitrification and the denitrification processes [3, 4]. The sensitive and reliable determination of nitrite is of interest in waste water processing [3, 4], and food analysis [5]. Its high toxicity is based mainly on the formation of carcinogenic nitroso compounds [5–7]. Nitrite is also formed by the oxydation of nitric oxide in many physiologic processes at the cellular level and is therefore of growing interest in clinical chemistry [8, 9].

Therefore, there is a great demand for sensitive, accurate and reliable determination methods.

Nitrite is most often determined photometrically by diazotization of aromatic amines and subsequent coupling, *e.g.* with N-(1-naphthyl)ethylenediamine [1, 8–10]. It can also be determined by chemiluminescence [11–13], fluorescence [14], amperometric [15] and biamperometric [16, 17] detection.

Berka et al. [18] and Spohn [19] developed volumetric and coulometric batch titration procedures, respectively, for the precise determination of nitrite based on its reaction with hydrazine in strongly acid media. The following stoichiometry was proposed for the determination reaction in strongly acid solutions.



Some contradictory results were published with respect to the stoichiometry and the reaction mechanism. According to Stanbury [20], and Prasad and Kumar [21] the reaction between nitrite and hydrazine generates a variety of products including  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  and  $\text{HN}_3$ . Perrott et al. [22] took into consideration the reaction of azide with nitrite according to Eq. (2). Besides reaction (1) the reactions (3) and (4) are proposed to occur under certain conditions. Doherty et al. [23] showed that under acid conditions 2-aminodiiminol ( $\text{NH}_2\text{N}=\text{NOH}$ )



is formed as an intermediate, which is further nitrosated leading to the formation of  $\text{N}_2\text{O}$  and  $\text{N}_2$  supporting the dominating role of reaction (1). Therefore and outgoing from earlier results [19, 24], the calibrationless coulometric flow titration [25] should be used to determine the stoichiometry and the required reaction time for the conversion of nitrite with hydrazine in strongly acid media.

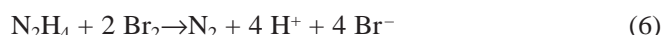
Because hydrazine can be coulometrically titrated with high resolution in low concentration solutions [19] a fur-

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ther aim of this paper was the development of an automatic backtitration procedure for nitrite. The principle of coulometric backtitration [19, 26] had to be combined with the triangle-programmed coulometric flow titration [24–31]. Fuhrmann et al. [25, 32, 33] and Becker et al. [34] demonstrated the possibility to perform accurate triangle-programmed flow titrations without calibration and to achieve accuracies and precisions comparable to those of coulometric batch titrations. To decrease the limit of titration (LOT), which is the lowest titratable amount of the analyte, the flow titration principle was combined with the highly sensitive chemiluminescence detection to follow the titration course. This detection method was compared with the amperometric end-point location.

According to the general reaction scheme (5) and reaction (6) and taking into consideration



the equivalence conditions the stoichiometric factors  $j$  and  $d$  can be determined by coulometric flow titration.  $a = 1$  and  $b = 2$  are the stoichiometric factors of reaction (6), on which the coulometric backtitration is based. The Eqs. (7) and (8) define the equivalence conditions for the reaction of the analyte ( $n_S$ ) and the reagent excess ( $n_E$ ) and for the reaction

$$dn_S = j (n_E - n_E') = d C_S V_S \quad (7)$$

$$2n_E' = n_R \quad (8)$$

of the remaining amount ( $n_E'$ ) of reagent with the titration reagent ( $n_R$ ), respectively.  $n_S$ ,  $n_E$ ,  $n_E'$  and  $n_R$  are the corresponding molar mass flow rates. For 100% current efficiency of the bromine generation and completeness of reaction (6) the correlation between the measured time difference  $\Delta t$  and the molar amount  $n_E$  of hydrazine can be expressed by Eq. (9). Equation (9) is the basic equation to describe the triangle-programmed coulometric flow titration [24, 33, 35] with number  $z$  of exchanged electrons per formula unit of the titration reagent, the Faraday constant  $F$ , the maximum of the electrolysis current  $I_{\max}$ , the time  $\Delta t = t_{\text{eq},2} - t_{\text{eq},1}$  between the two equivalence points  $t_{\text{eq},1}$  and  $t_{\text{eq},2}$ , and the time  $2\tau$ , during which the concentration triangle of the titration reagent is generated. According to Fuhrmann and Spohn [33],  $f$  describes the deviation of the measured from the ideal isosceles triangle of the electro-generated reagent concentration with the basis  $2\tau$ . From Eq. (9) the Eqs. (10) and (11) can be derived, which describe the flow titration

$$n_E = a/b \cdot I_{\max}/(Fz) \cdot [1 - \Delta t/(2\tau f)] \quad (9)$$

of the added amount  $n_E$  of hydrazine and the remained excess  $n_E'$  of this reagent [26, 29, 34] with the time differences  $\Delta t$  and  $\Delta t'$  between the corresponding equivalence points.

$$n_E = 0.25 I_{\max}/F \cdot [1 - \Delta t/(2\tau f)] \quad (10)$$

$$n_E' = 0.25 I_{\max}/F \cdot [1 - \Delta t'/(2\tau f)] \quad (11)$$

Equation (12) follows from Eqs. (7–11) with the difference  $\Delta \Delta t = \Delta t' - \Delta t$  between the measured time differences, which is proportional to analyte concentration  $C_S$ , and the volumetric flow rate  $V_S$  of the sample solution.

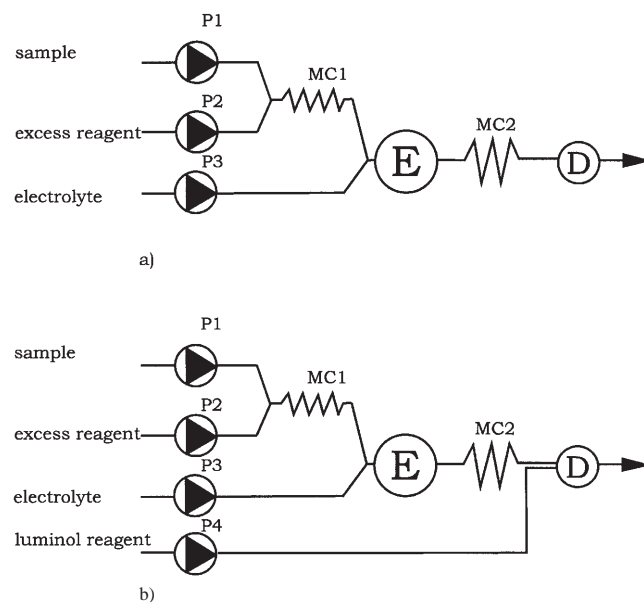
$$C_S = 0.25 j/d \cdot I_{\max}/(FV_S) \cdot \Delta \Delta t/(2\tau f) \quad (12)$$

## Experimental

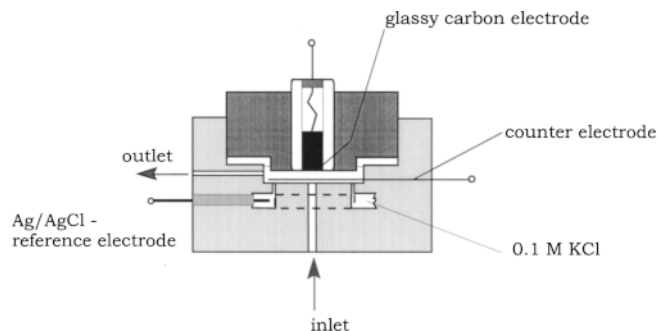
**Reagents.** All chemicals were of analytical grade and from Sigma (Deisenhofen, Germany) or Fluka (Buchs, Switzerland). A 10.0 mM hydrazine stock solution was prepared by dissolving 1.301 g hydrazinium hydrogensulfate in water and filling up to 1 L. The coulometric titration with bromine against a biamperometric end-point confirmed this hydrazine concentration. An 80 mM nitrite stock standard solution was prepared by dissolving 1.380 g of  $\text{NaNO}_2$  in water and filling up to 250 mL. The corresponding standard solutions were prepared by subsequent dilution of the stock solutions with doubly distilled, deionized water immediately before use.

1 mmol Luminol and 5  $\mu\text{mol}$   $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were dissolved in 1 L of 0.1 M  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  buffer solution, adjusted to pH = 10 to prepare the chemiluminescence reagent.

**Measuring set-up.** Figures 1 a and b show the measuring set-ups of the coulometric backtitration with amperometric and chemiluminescence end-point location, respectively. The electrolyte, the sample and the indicator solution were propelled by computer-controlled piston pumps (Dosimat 665, Metrohm, Herisau, Switzerland). PTFE tubes with an inner diameter of 0.5 mm were used to connect the pumps, the electrolysis cell, the knotted type tube reactors MC1 and MC2, and the flow detector D. The sample solution is mixed with an excess of the reagent hydrazine in the reactor MC1 with a tube diameter of 0.8 mm. Then the resulting solution is mixed with the flowing electrolyte, which contains 0.5 M KBr. The titrant bromine is electrogenerated on a platinum wire electrode with an effective length of 11 mm and a diameter of 0.5 mm. The electrolysis cell E was described earlier [24] and



**Fig. 1** Measuring set-ups for coulometric backtitrations with **a** – amperometric and **b** – chemiluminescence detection of the titration curves,  $E$  – flow electrolysis cell,  $D$  – flow detector,  $P1$ – $P4$  – pumps,  $MC1$  and  $MC2$  (tube length: 30 mm, tube diameter: 0.5 mm) knotted type tube reactors



**Fig. 2** Amperometric wall-jet detector cell

manufactured from KelF. The generator electrode is mounted into the outlet channel with a diameter of 0.8 mm. The counter electrode is a coiled Pt wire with a diameter of 0.5 mm and a length of 50 mm placed into a 0.5 mL chamber filled with 0.5 M NaBr, which is separated from the electrolyte channel by a cationic exchange membrane.

The nonconsumed bromine is detected amperometrically or chemiluminometrically in the corresponding flow detector D. Figure 2 shows the amperometric flow detector cell, which was connected to a home made potentiostat. The amperometric detector was similar to that described by Appelqvist et al. [36]. The indicator electrode was a glassy carbon electrode with a diameter of 3 mm and polarized at 0 mV *versus* an Ag/AgCl/0.1 M KCl reference electrode.

The chemiluminescence detector cell was described earlier [24] in more detail. The electrolyte, in which the determination reaction is taking place, is flowing into a central quartz capillary with an inner diameter of 0.32 mm. The luminol indicator solution is flowing through an outer tube of PTFE with an inner diameter of 0.8 mm. The electrolyte and the indicator solution are mixed in a jet chamber, the volume of which is approximately adjusted to 2.5  $\mu$ L. A miniaturized photomultiplier PMT (Hamamatsu H5774, Japan) is placed behind a glass plate of a thickness of 1 mm with the optical window focused on the outlet of the inner quartz capillary.

The measuring set-ups were controlled automatically by a Personal Computer (PC) on the basis of the earlier described program CET 3 (Control and Evaluation of Titration) [31, 32], which performs also the automatic evaluation of the flow titration curves.

**Reference method.** To validate the proposed coulometric nitrite determination the photometric FIA (Flow Injection Analysis) procedure described by McCormack et al. [10] was applied as the reference method. These authors worked out this method for the analysis of river water. The thoroughly validated method is based on the reaction of nitrite sulfanilamide followed by the diazotization with (N-(1-naphthyl)ethylenediamine in phosphoric acid. The resulting dye was detected at 540 nm in a photometric flow detector (UVIS 200, Linear Instruments, USA).

## Results and discussion

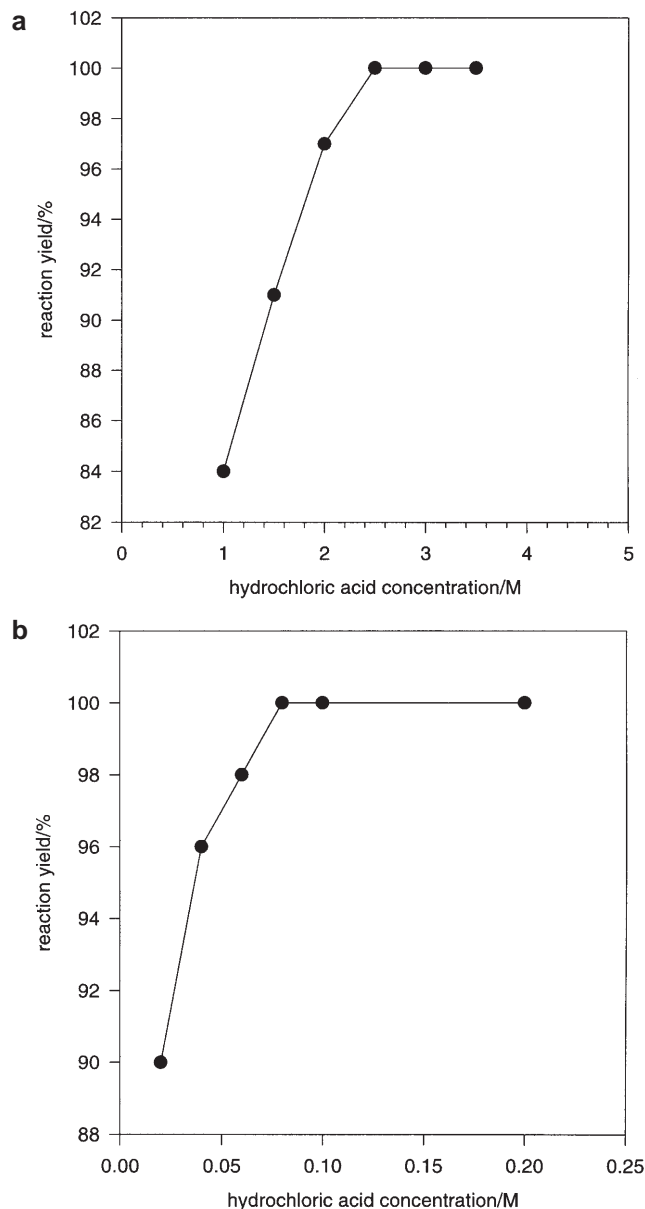
### Coulometric flow titration of hydrazine

As demonstrated earlier [37] hydrazine can be determined precisely by the coulometric flow titration with electrogenerated bromine without calibration. The measured slope factors and the measured  $\Delta t$  values are almost equal to the precalculated values both in experiments using the chemiluminescence and the amperometric detection in two different concentration ranges of hydrazine. Systematic errors between 8.0% and 0.8% occur for the chemiluminescence

detection without calibration in the investigated concentration range between 0.06 and 25.3  $\mu$ M. The amperometric detection provides without calibration systematic errors between 9.0 and 0.2% in the range between 0.2 and 25  $\mu$ M. The relative standard deviations are between 2.7% and 0.2% calculated for six parallel titrations. The precision and reliability of the coulometric flow titration of hydrazine is the basis for the accurate determination of nitrite by the proposed backtitration procedure.

### Reaction between hydrazine and nitrite

The reaction between hydrazine and nitrite was investigated both under flow conditions in MC1 (Fig. 1) at dif-



**Fig. 3** Dependencies of the degree of nitrite elimination on the hydrochloric acid concentration, **a** – measured under flow conditions for a residence times of 204 s and **b** – measured under batch conditions for a residence time of 30 min

ferent residence times and batch conditions. Nitrite does not react with bromine under the investigated conditions. Figure 3a shows the dependence of the apparent degree of nitrite consumption by hydrazine, defined as the ratio between the consumed to the initial concentration of nitrite, on the HCl concentration in reactor MC1. Figure 3b demonstrates the corresponding dependence for a residence time of 30 min in an incubation volume of 25 mL. The nitrite concentrations have been calculated from the remaining and initial hydrazine concentrations, which were determined by coulometric flow titration with electrogenerated bromine with amperometric end-point detection. The calculations were based on the stoichiometry of reactions (1) and (6). At a residence time of 204 s in MC1, the HCl concentration must be higher than 2.5 M to achieve a constant nitrite consumption. The decrease of the nitrite concentration was equal to that calculated according to Eq. (12) assuming reaction (1). The HCl concentration was adjusted to 3 M in MC1 at a residence time of 204 s for the following flow titration experiments with in-line nitrite conversion. Under batch conditions and at a residence time of 30 min, a complete elimination of nitrite can be achieved at HCl concentrations higher than 0.08 M.

The stoichiometric factors  $d$  and  $j$  were determined both under flow and batch conditions by coulometric titration to amperometrically detected equivalence points. Stoichiometric factors of  $d = 1.01 \pm 0.01$  and  $d = 1.00 \pm 0.02$  were measured ( $n = 5$ ) under batch and flow conditions, respectively. The corresponding factors for nitrite were  $j = 2.00 \pm 0.03$  and  $2.01 \pm 0.04$  ( $n = 5$ ) under batch and flow

conditions, respectively. Both experiments confirmed the stoichiometry of reaction (1).

#### Determination of nitrite by coulometric backtitration procedures

The nitrite containing sample solution is mixed continuously with a standardized hydrazine solution in 6 M HCl. The hydrazine concentration was determined before by a coulometric batch titration or by coulometric flow titration between the backtitrations. The latter method should be used for hydrazine concentrations below 0.1 mM. The sample concentration is calculated automatically either from the measured time difference  $\Delta t'$  and the known hydrazine concentration or from the difference  $\Delta \Delta t$  between the two measured time differences  $\Delta t'$  and  $\Delta t$  according to Eq. (12).

In a first series of experiments the primary reaction between nitrite and hydrazine took place in the batch incubation vessel under the above mentioned conditions. Then the remaining hydrazine concentration is determined by coulometric flow titration either with chemiluminescence or amperometric detection. Between 0.1 and 50  $\mu\text{M}$  nitrite were determined by using the chemiluminescence detection with a maximum electrolysis current between 0.1 mA and 0.01 mA at  $2\tau = 120$  s. Between 0.25 and 30  $\mu\text{M}$  nitrite was determined precisely by using the amperometric end-point location (Table 1).

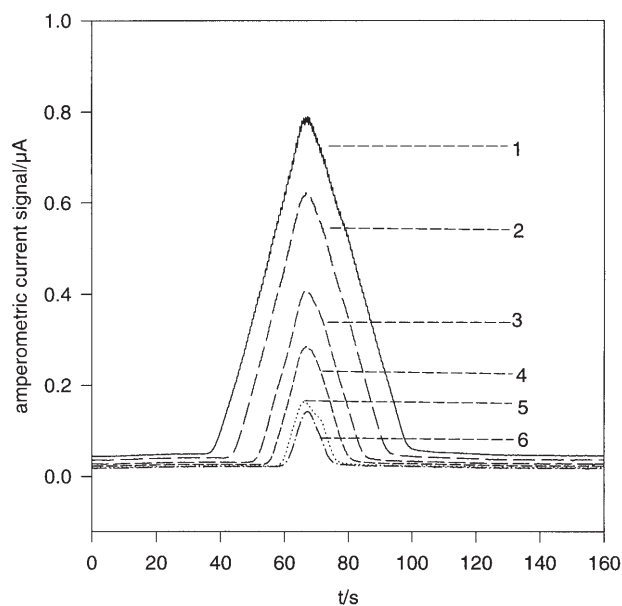
Table 2 summarizes some flow titration results obtained by using the in-line conversion of nitrite with hy-

**Table 1** Results of the triangle-programmed coulometric backtitration with chemiluminescence and amperometric detection of the equivalence points to determine nitrite after its reaction with known hydrazine amounts in a batch reactor,  $2\tau = 120$  s,  $V_S = 0.50$  mLmin<sup>-1</sup>

Range $\mu\text{M}$	[NH <sub>2</sub> NH <sub>2</sub> ] $\mu\text{M}$	$I_{\text{max}}/\mu\text{A}$		Correlations between $\Delta t$ and $C_S$	$r^2, n = 6$ $\alpha = 0.05$	$f$
Chemiluminescence detection						
1.60–50.0	32.0	120	measured	$\Delta \Delta t = \Delta t' - 17.5$ s = 1.61 $\mu\text{M}^{-1}C_S$	0.9998	1.00
			calculated	$\Delta \Delta t = \Delta t' - 17.1$ s = 1.61 $\mu\text{M}^{-1}C_S$		
0.10–3.20	3.00	12.0	measured	$\Delta \Delta t = \Delta t' - 23.3$ s = 16.3 $\mu\text{M}^{-1}C_S$	0.9995	1.01
			calculated	$\Delta \Delta t = \Delta t' - 23.5$ s = 16.1 $\mu\text{M}^{-1}C_S$		
Amperometric detection						
1.00–30.0	32.0	120	measured	$\Delta \Delta t = \Delta t' - 17.5$ s = 1.61 $\mu\text{M}^{-1}C_S$	0.9992	1.00
			calculated	$\Delta \Delta t = \Delta t' - 17.1$ s = 1.61 $\mu\text{M}^{-1}C_S$		
0.25–2.00	3.00	12.0	measured	$\Delta \Delta t = \Delta t' - 24.7$ s = 15.7 $\mu\text{M}^{-1}C_S$	0.9993	0.975
			calculated	$\Delta \Delta t = \Delta t' - 23.5$ s = 16.1 $\mu\text{M}^{-1}C_S$		

**Table 2** Results of the triangle-programmed coulometric backtitration with amperometric detection of the equivalence points to determine nitrite after its in-line conversion with known hydrazine amounts in a batch reactor,  $2\tau = 120$  s, [HD] = hydrazine concentration

[NO <sub>2</sub> <sup>-</sup> ] $\mu\text{M}$	[HD] $\mu\text{M}$	$I_{\text{max}}/\mu\text{A}$		Correlations between $\Delta t$ and $C_S$	$r^2, n = 6$ $\alpha = 0.05$	$f$	$V_S$ mLmin <sup>-1</sup>
10.0–65.0	85.0	120	meas.	$\Delta \Delta t = \Delta t' - 37.6$ s = 0.485 $\mu\text{M}^{-1}C_S$	0.9996	1.01	0.15
			calc.	$\Delta \Delta t = \Delta t' - 38.0$ s = 0.482 $\mu\text{M}^{-1}C_S$			
0.10–6.00	5.34	15.0	meas.	$\Delta \Delta t = \Delta t' - 58.2$ s = 3.86 $\mu\text{M}^{-1}C_S$	0.9988	1.00	
			calc.	$\Delta \Delta t = \Delta t' - 58.2$ s = 3.86 $\mu\text{M}^{-1}C_S$			
1.00–30.0	30.9	120	meas.	$\Delta \Delta t = \Delta t' - 16.4$ s = 1.60 $\mu\text{M}^{-1}C_S$	0.9992	0.994	0.50
			calc.	$\Delta \Delta t = \Delta t' - 17.1$ s = 1.61 $\mu\text{M}^{-1}C_S$			
0.25–2.00	2.85	12.0	meas.	$\Delta \Delta t = \Delta t' - 23.5$ s = 16.2 $\mu\text{M}^{-1}C_S$	0.9993	1.01	
			calc.	$\Delta \Delta t = \Delta t' - 23.5$ s = 16.1 $\mu\text{M}^{-1}C_S$			



**Fig. 4** Amperometric titration curves 1–6 recorded for 30.0, 20.0, 10.0, 5.0, 1.0 and 0.0  $\mu\text{M}$  nitrite, respectively; hydrazine concentration: 32.0  $\mu\text{M}$ ,  $2\tau = 120$  s,  $V_s = 0.5$   $\text{mLmin}^{-1}$ ,  $I_{\text{max}} = 120$   $\mu\text{A}$

drazine. For this procedure only the amperometric detection could be applied to detect the equivalence points. An excellent agreement between precalculated working lines and the measured calibration graphs were obtained, which demonstrates again the possibility to work without calibration. Figure 4 shows a series of amperometric backtitration curves for different nitrite concentrations recorded at the same excess of hydrazine demonstrating a high degree of linearity between the detector signal and the electrogenerated bromine concentration. This simplifies the automated evaluation of the titration curves.

To perform the nitrite/hydrazine reaction under in-line flow conditions only the amperometric end-point detection could be applied, because the high acid concentration causes a strong carbon dioxide release disturbing the chemiluminescence detection. Between 0.25 and 65  $\mu\text{M}$  of nitrite can be determined precisely by using the amperometric end-point detection. For five successive titrations the relative standard deviation is between 0.2 and 0.4% for titration of 0.25  $\mu\text{M}$  nitrite.

#### Determination of nitrite in river and tap water

Performing the nitrite reduction in reactor MC1 (Fig. 1) the amperometric flow titration procedure was applied to the determination of low concentrations of nitrite in river and in tap water.

The water samples from the river Saale (Halle, Germany) were filtered through a paper membrane. The tap water sample can be titrated without sample treatment. For both kinds of samples the accuracy of the proposed nitrite determination procedure was examined by recov-

**Table 3** Analysis of tap and river water samples for nitrite by coulometric backtitration of hydrazine and photometric detection under FIA conditions

Sample	Found $\mu\text{M}$		Added $\mu\text{M}$	Total $\mu\text{M}$	Recovered $\mu\text{M}$	Recovery %
	Coul.	FIA phot.				
Tap water						
1	0	0	3.0	3.0	3.0	100
			16.0	15.8	15.8	98.7
2	0	0	3.0	3.1	3.1	103
			16.0	16.0	16.0	100
3	0	0	3.0	2.8	2.8	93
			16.0	16.1	16.1	101
4	0	0	3.0	2.9	2.9	97
			16.0	15.5	15.5	96.9
Mean recovery						98.7
River water						
1	10.5	10.6	3.0	13.5	3.0	100
			16.0	26.2	15.7	98.7
2	13.5	13.4	3.0	16.7	3.2	107
			16.0	29.6	16.1	101
3	15.4	15.4	3.0	18.3	2.9	97
			16.0	31.2	15.8	98.7
4	10.1	10.2	3.0	12.9	2.8	93
			16.0	25.9	15.8	98.7
Mean recovery						99.3

ery experiments. In tap water samples recoveries of 97–101% and 93–103% were determined for 16 and 3  $\mu\text{M}$  of added nitrite, respectively. In river water samples similar mean recoveries of 98.7–101 and 93–107% were found for 16 and 3  $\mu\text{M}$  of nitrite, respectively, added to river water. At 10  $\mu\text{M}$  of nitrite the relative standard deviation was determined to be 0.24% for tenfold repeated flow titrations of spiked river water. The tap water did not contain detectable nitrite concentrations. The mean concentration of nitrite in four river water samples, which were taken at the same position sequentially, was 12.4  $\mu\text{M}$ , found both by the coulometric backtitration procedure and the photometric reference procedure. There is an almost perfect agreement between the photometrically and the coulometrically determined nitrite concentrations in the river water samples (Table 3).

#### Conclusions

The quantitative reduction of nitrite by hydrazine in hydrochloric acid solutions can be used as the basis for a calibrationless flow backtitration procedure to determine micromolar concentrations of nitrite. Because nitrite does not react with bromine in strongly acid solutions, the backtitration of the hydrazine excess with coulometrically generated bromine to an amperometrically indicated end-point is reliable and accurate under flow conditions. The excess of reagent can easily be standardized by the coulometric flow titration of hydrazine.

It can be expected that the proposed concept of coulometric backtitrations in a flow through channel can also be applied to many other determinations, *e.g.* the determination of peroxodisulfate and other oxidants after their conversion with iodide to triiodide and the backtitration of an added excess of thiosulfate or arsenite by electrogenerated triiodide. Coulometric backtitrations can be performed under flow conditions in capillary tubes and easily be automatized.

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