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## Redox-iodometry: a new potentiometric method

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**Abstract** A new iodometric method for quantifying aqueous solutions of iodide-oxidizing and iodine-reducing substances, as well as plain iodine/iodide solutions, is presented. It is based on the redox potential of said solutions after reaction with iodide (or iodine) of known initial concentration. Calibration of the system and calculations of unknown concentrations was performed on the basis of developed algorithms and simple GWBASIC-programs. The method is distinguished by a short analysis time (2–3 min) and a simple instrumentation consisting of pH/mV meter, platinum and reference electrodes. In general the feasible concentration range encompasses 0.1 to  $10^{-6}$  mol/L, although it goes down to  $10^{-8}$  mol/L (0.001 mg  $\text{Cl}_2/\text{L}$ ) for oxidants like active chlorine compounds. The calculated imprecision and inaccuracy of the method were found to be 0.4–0.9% and 0.3–0.8%, respectively, resulting in a total error of 0.5–1.2%. Based on the experiments, average imprecisions of 1.0–1.5% at  $c(\text{Ox}) > 10^{-5}$  M, 1.5–3% at  $10^{-5}$  to  $10^{-7}$  M, and 4–7% at  $< 10^{-7}$  M were found. Redox-iodometry is a simple, precise, and time-saving substitute for the more laborious and expensive iodometric titration method, which, like other well-established colorimetric procedures, is clearly outbalanced at low concentrations; this underlines the practical importance of redox-iodometry.

**Keywords** Redox potential · Oxidation capacity · Iodometric titration · Colorimetric methods

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### Introduction

A very substantial improvement in iodometric titration was the introduction of the redox potential as an indicator, where the endpoint is signified by the inflection point of the redox-potential versus titrant volume curve. The redox-potential, however, was also used in non-titrimetric analytic procedures. In 1978 Rigdon et al [1] introduced a potentiometric method for residual chlorine using both iodide-sensitive and platinum electrodes together with a multiple addition procedure for an iodide standard. The same electrodes were used by Gottardi [2] for the plain potentiometric measurement of free molecular iodine in povidone-iodine preparations. A single measurement of the redox-potential combined with the titrimetrically-assessed oxidation capacity was used to measure equilibrium concentrations of the most important iodine species in aqueous iodine solutions [3].

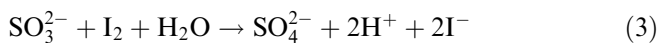
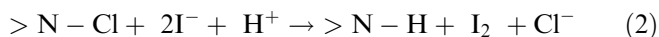
Contrary to the quoted papers, which consider *equilibrium concentrations* in iodine solutions, this study presents a straightforward iodometric method for measuring the *oxidation (or reduction) capacity* of all kinds of iodide-oxidizing and iodine-reducing substances. Benefits include the very simple equipment required (stirred vessel, platinum and reference electrodes), the short analysis time, and the lack of titration.

### Method

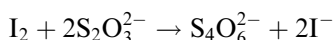
Oxidants, which react quantitatively with iodide according to Eq. 1, can be assayed on the basis of the liberated iodine.



On the other hand, the reverse of Eq. 1 concerns the assessment of a reducing agent whose concentration is related to the consumed amount of surplus iodine. Common examples of both implementations are shown in Eqs. 2 and 3



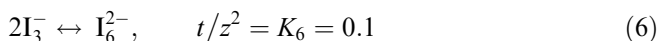
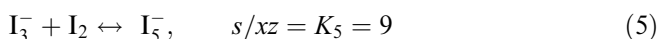
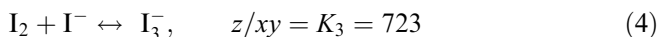
where the generated or consumed iodine is measured by titration (for example with thiosulphate):



In both cases the titration step can be dispensed with if the initial iodide (or iodine and iodide) concentration and the redox-potential,  $E_{\text{red}}$ , of the resulting iodine/iodide solution are known. This allows us to calculate the total iodine concentration of the solution, which parallels the oxidation (or reduction) capacity of the sample.

The quantitative transformation of the oxidation capacity into iodine,  $c(\text{Ox}) \rightarrow c(\text{I}_2)$ , requires the presence of surplus iodide. Therefore, virtually no iodate formation takes place [4] and loss of  $\text{I}_2$  by evaporation is minimized. The same considerations also apply to the assessment of reducing substances.

Additionally, if the pH is kept below 7, only the five species  $\text{I}_2$ ,  $\text{I}^-$ ,  $\text{I}_3^-$ ,  $\text{I}_5^-$  and  $\text{I}_6^{2-}$  are of importance [5], the equilibrium concentrations of which we will abbreviate by  $x = [\text{I}_2]$ ,  $y = [\text{I}^-]$ ,  $z = [\text{I}_3^-]$ ,  $s = [\text{I}_5^-]$ , and  $t = [\text{I}_6^{2-}]$ . They are governed by the pH-independent equilibria Eqs. 4–6 [6, 7], with three corresponding equilibrium constants.



The effective concentrations of iodine and iodide are apparently

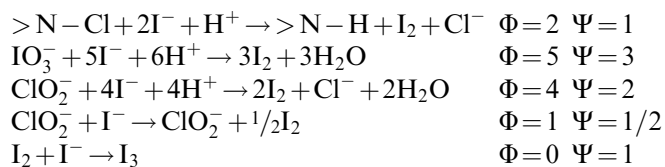
$$c(\text{I}_2)_{\text{eff}} = x + z + 2s + 2t \quad (7)$$

$$c(\text{I}^-)_{\text{eff}} = y + z + s + 2t \quad (8)$$

#### Measurement of oxidants (*Algorithm 1*)

A defined volume of an iodide solution of known concentration is added to a defined volume of the solution of the oxidant. It yields the initial concentration  $c(\text{I}^-)$ . After the reaction is completed, enough iodide should still be present to ensure total dissolution of the emerging iodine (see Eqs. 4–6).

Because of the manifold stoichiometry of the reaction of oxidants with iodide, it was necessary to introduce the coefficients  $\Phi$  and  $\Psi$ , which refer to the number of consumed iodide ions and the produced equivalents of iodine, respectively, after reduction of one mole of the oxidant. In the reactions listed below, the ranges are  $\Phi=0-5$  and  $\Psi=1/2-3$ .



The effective concentrations of iodine and iodide before (index 1) and after (index 2) the reaction is completed, with  $c(\text{I}_2)_1=0$ , are

$$c(\text{I}_2)_2 = \Psi^* c(\text{Ox}) \quad (9)$$

$$c(\text{I}^-)_2 = c(\text{I}^-)_1 - \Phi^* c(\text{Ox}) \quad (10)$$

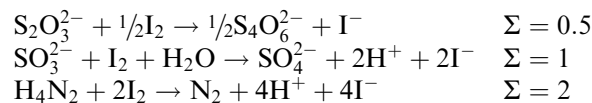
where  $c(\text{Ox})$  is the (unknown) molar concentration of the oxidant. Its elimination yields the mass-balance

$$\Psi c(\text{I}^-)_1 = \Psi y + \Phi x + (\Phi + \Psi)z + (2\Phi + \Psi)s + 2(\Phi + \Psi)t \quad (11)$$

Equation 11, together with the measured redox-potential  $E_{\text{red}}$ , the initial iodide concentration  $c(\text{I}^-)_1$ , and the standard value  $E_0^*$  (see “Calibration”), forms the basis for the calculation of  $c(\text{Ox})$ , which is laid down in *Algorithm 1* (see “Supporting Information”).

#### Measurement of reducing substances (*Algorithm 1a*)

A defined volume of an iodine/iodide solution with known concentrations is added to a defined volume of the solution of the reducing agent. It yields the initial concentrations  $c(\text{I}_2)$  and  $c(\text{I}^-)$ . After completion of the reaction, sufficient iodine should still be present. From the stoichiometric formulae for the reaction of iodine with thiosulphate, sulfite, and hydrazine, it follows that the number of iodine molecules ( $\Sigma$ ) that are consumed by one molecule of the reducing compound can range between 0.5 and 2, while the number of iodide ions formed comes to  $2\Sigma$ .



In analogy to Eqs. 9 and 10, the mass-balances Eqs. 12 and 13 can be defined, with  $c(\text{Red})$  signifying the molar concentration of the reducing agent.

$$c(\text{I}_2)_2 = c(\text{I}_2)_1 - \Sigma * c(\text{Red}) \quad (12)$$

$$c(\text{I}^-)_2 = c(\text{I}^-)_1 + 2\Sigma * c(\text{Red}) \quad (13)$$

and, by elimination of  $c(\text{Red})$

$$c(\text{I}^-)_1 + 2c(\text{I}_2)_1 = y + 2x + 3z + 5s + 6t \quad (14)$$

which does not contain the stoichiometric coefficient  $\Sigma$ .

Equation 14, together with  $E_{\text{red}}$ ,  $E_0^*$ ,  $c(\text{I}^-)_1$ , and  $c(\text{I}_2)_1$ , forms the basis for the calculation of  $c(\text{Red})$ , which is laid down in *Algorithm 1a* (see “Supporting Information”).

### Measurement of plain iodine/iodide solutions (Algorithm 2)

Algorithm 1 is not capable of measuring iodine solutions unless the total iodide concentration,  $c(\text{I}^-)$ , is known. If this is not the case, its oxidation capacity,  $c(\text{I}_2)$ , can be determined by two measurements of the redox-potential, before ( $E_1$ ) and after ( $E_2$ ) addition of a known iodide increment,  $\Delta$ , which is defined by the dilution factor,  $\Omega$ , yielding Eqs. 15 and 16.

$$c(\text{I}_2)_2 = \Omega * c(\text{I}_2)_1 \quad (15)$$

$$c(\text{I}^-)_2 = \Omega * c(\text{I}^-)_1 + \Delta \quad (16)$$

Equations 15 and 16, together with Eqs. 4–8, along with the potentials  $E_1$ ,  $E_2$ ,  $E_0^*$ , and with the characteristics of the iodide increment,  $\Delta$ , and  $\Omega$ , form the basis for the calculation of the total iodine concentration of the sample,  $c(\text{I}_2)_1$ , which is laid down in *Algorithm 2* (see “Supporting Information”).

### Calibration (Algorithm 3)

The standard value  $E_0^*$  comprises the potential  $E_{\text{red}}$  of the redox reaction  $\text{I}_2 + 2\text{e}^- \leftrightarrow 2\text{I}^-$ , the potential of the reference electrode ( $E_{\text{ref}}$ ), and its liquid junction potential ( $E_j$ ):

$$E_0^* = E_{\text{red}} - E_{\text{ref}} - E_j$$

$E_{\text{red}}$  is clearly defined, for a chosen temperature, by the Nernst equation

$$E_{\text{red}} = E_{0, \text{I}_2/\text{I}^-} - S \log \left( \frac{[\text{I}^-]^2 f^2}{[\text{I}_2]} \right) \quad (17)$$

where  $E_{0, \text{I}_2/\text{I}^-} = 622.4$  mV,  $S = 29.58$  mV/decade at 25 °C, and  $f$  is the activity coefficient.  $E_{\text{ref}}$  and  $E_j$ , however, are also influenced by the concentration of the salt bridge, and they are generally not known exactly.

From the expressions for the measured and calculated redox-potentials of the standardizing solution

$$E_{\text{meas}} = E_{0, \text{I}_2/\text{I}^-} - S \log \left( \frac{[\text{I}^-]^2 f^2}{[\text{I}_2]} \right) - E_{\text{ref}} - E_j$$

$$E_{\text{calc}} = E_{0, \text{I}_2/\text{I}^-} - S \log \left( \frac{[\text{I}^-]^2 f^2}{[\text{I}_2]} \right)$$

it follows easily that the sum of the unknown potentials comes to

$$E_{\text{ref}} + E_j = E_{\text{calc}} - E_{\text{meas}}$$

which can be transformed to Eq.

$$E_0^* = E_{\text{meas}} + S \log(y^2/x) \quad (18)$$

where  $[\text{I}^-]$  and  $[\text{I}_2]$  are the equilibrium concentrations calculated with *Algorithm 3* (see “Supporting Information”). Since the measurements are performed at a high, nearly constant, ionic strength (see below), the activity coefficient can be waived.

### Measurement of real samples

For samples of, say, industrial process water or seawater, the exact composition is not known and differentiating the individual iodide-oxidizing or iodine-reducing constituents and their molar concentrations is not possible. However, as is the case with iodometric titration, the reaction pH chosen (see also “Discussion”) determines which components are included, and the result is specified as oxidation capacity, iodometrically acquired at a given pH.

## Experimental

### Measurement at constant ionic strength

Since the ionic strength of the samples is, in general, unknown, it was necessary to work with a superimposed high ionic strength achieved by addition of a “Total Ionic Strength Adjusting Buffer” (TISAB solution) to modify the sample and standard. The high ionic strength also prevents any impairment of the accuracy caused by leakage of chloride from the reference electrode. Because the reactions with iodide consume or produce protons (see Eqs. 2 and 3), the TISAB solution must contain a pH buffer. Phosphate was used for pH 2–3 and pH 6–7, acetate for pH 4–5, and *tris*-(hydroxymethyl) aminomethane (Tris) for pH 8.0–8.2.

### Instrumentation

A mV/pH meter (PHM250 Ion Analyzer, Radiometer, Copenhagen) was used, as well as a thermostated reaction vessel (50 mL) with magnetic stirrer and a covering with four apertures, three containing the electrodes (platinum electrode M21PT, pH-electrode PHG201-7, reference electrode REF 401, all from Radiometer) and one for adding reagents. Iodometric titrations were performed with a TitraLab TIM900 and a 2 mL ABU901 Autoburette, all from Radiometer. Exact volumes of sample and reagents were extracted with both 100–1000 and 500–5000  $\mu\text{L}$  research pipettes from Eppendorf.

### Chemicals and solutions

All chemicals were of GR quality and purchased from Merck, Darmstadt. Potassium iodate was also recrystallized from hot water.

### Iodide solutions

Aqueous solutions of 1.000, 0.500, and 0.100 M KI, each with 0.05 M NaOH (1 pellet/100 mL) were used. The resulting alkaline milieu, pH 12.7, ensures long-term suppression of iodide oxidation from the oxygen in the air.

### Iodine solutions

Aqueous solutions containing 0.100 mol iodine and 1.000 M KI (without the addition of NaOH) were used.

### TISAB solutions

TISAB I was used when working at pH 2.2 (achieved through 2 M sodium dihydrogen phosphate + 2 M NaNO<sub>3</sub> adjusted with sulfuric acid to pH 2.0); TISAB II was used when working at pH 4.5 (achieved through 3.5 M NaNO<sub>3</sub> + 1 M acetic acid + 0.5 M NaOH); TISAB III was used when working at pH 6.6 (high dilutions; achieved through 1 M disodium hydrogen phosphate + 1 M sodium dihydrogen phosphate + 2 M NaNO<sub>3</sub>); TISAB IV was used when working at pH 8.2 (achieved through 1 M Tris-buffer + 3 M NaNO<sub>3</sub> adjusted with hydrochloric acid to pH 8.0).

### Measuring the redox-potential

Using the auto-read function, with the stability criterium tuned to 0.1 mV/min (time 5.0 min), the redox-potential was taken after it had practically settled. For standard measurements, the stability criterium was tuned to 0.2 mV/min, which enabled shorter measuring times with slightly less precision. The auto-read function has the advantage that the sample temperature set does not need to be observed. Constant redox-potential ensures that the final temperature is reached. All measurements (and calibrations) were performed at 25.0 °C.

### Procedure A (oxidants and reducing agents)

3000 µL of the appropriate TISAB solution and 1000 µL of the iodide solution (oxidants) or iodine solution (reducing agents) was added to 3000 µL of the sample placed in the reaction vessel, giving a total volume of 7 mL, which is a good compromise between precisely dispensed volumes and minor consumption of reagents. The redox-potential was measured as described above.

If necessary an “in situ dilution” of the sample was performed by supplementing a smaller sample with water up to 3000 µL.

### Procedure B (oxidants)

For very low concentrations of oxidants ( $< 10^{-5}$  M), 10,000 µL of the sample, 1000 µL of TISAB III, and 1000 µL of the 0.100 M iodide solution were used.

### Procedure C (iodine solutions)

The redox-potential of a mixture of 3000 µL of the sample and 3000 µL TISAB II was measured before ( $E_1$ )

and after ( $E_2$ ) addition of the iodide increment in the form of 1000 µL of iodide solution at a concentration high enough to induce a potential drop of at least 10 mV.

### Calibration

Measurement and calibration were always performed using the same procedure with the same TISAB solution.

- Weighed samples of resublimed iodine (20–50 mg) were transferred to the vessel and covered with 1000 µL 1 M KI. After complete dissolution, 3000 µL H<sub>2</sub>O and 3000 µL TISAB (I–IV) were added, and the redox-potential was measured.
- It turned out to be much simpler to measure the redox-potential of the mixture of H<sub>2</sub>O, TISAB, and 1000 µL of the iodine/iodide solution. This mode is especially recommended for reducing agents and low concentrations of oxidants.
- For KIO<sub>3</sub>, we used either weighed samples (5–14 mg) dissolved in 3000 µL H<sub>2</sub>O, or 3000 µL of a standard solution with 0.002–0.003 M KIO<sub>3</sub>. Both solutions were completed with 3000 µL TISAB I and 1000 µL iodide reagent.

### Calculation

The concentration of oxidant was calculated from the standard value,  $E_0^*$ , the measured redox-potential,  $E_{\text{red}}$ , and the initial iodide concentration,  $c(\text{I}^-)$ . Algorithm 1 was applied using the corresponding coefficients  $\Phi$  and  $\Psi$ . The concentration of reducing agent was calculated from  $E_0^*$ ,  $E_{\text{red}}$ , and the initial iodine and iodide concentrations,  $c(\text{I}_2)$  and  $c(\text{I}^-)$ , using Algorithm 1a with the appropriate coefficient  $\Sigma$ . The concentration of the iodine solution was calculated from  $E_0^*$ , the potentials  $E_1$  and  $E_2$ , and the characteristics of the iodide increment,  $\Delta$ , and  $\Omega$ , using Algorithm 2. The determination of  $E_0^*$  was performed with Algorithm 3 (iodine:  $\Phi=0$ ,  $\Psi=1$ ; iodate:  $\Phi=5$ ,  $\Psi=3$ ).

The calculations were performed with GWBASIC programs, which contained the necessary inputs for the potentials, volumes, and concentrations.

### Analysis of hypochlorite and chlorite in chlorine bleach (NaOCl)

- An amount of 3000 µL of the 20-fold- to 50-fold-diluted NaOCl solution (for example, 12% Cl<sup>+</sup>) was added to a mixture of 3000 µL TISAB-I and 1000 µL iodide solution (1.00 M KI). This order had to be maintained in order to avoid the formation of elemental chlorine by disproportionation caused by the high chloride content of commercial chlorine bleach at the operating pH of 2.2–2.4 ( $\text{HOCl} + \text{Cl}^- + \text{H}^+$

→ Cl<sub>2</sub> + H<sub>2</sub>O). Because chlorite also reacts with iodide under these conditions, the result,  $c(\text{Ox})_{\text{pH}2}$ , calculated with  $\Phi=2$  and  $\Psi=1$ , concerns both compounds according to  $c(\text{Ox})_{\text{pH}2} = c(\text{OCl}^-) + 2c(\text{ClO}_2^-)$ .

- b. The same procedure was performed with TISAB IV and following the same order of reagent addition, in this case to prevent oxidation of the Tris buffer by hypochlorite, which, however, is stable against iodine. Since chlorite reacts with iodide at pH 8.2 very slowly, the result predominantly concerns hypochlorite:  $c(\text{Ox})_{\text{pH}8} = c(\text{OCl}^-)$ . The concentration of chlorite is then  $c(\text{ClO}_2^-) = 1/2[c(\text{Ox})_{\text{pH}2} - c(\text{Ox})_{\text{pH}8}]$ .

## Statistics

Calculations and graphs were done with GraphPad PRISM, Version 4.00. The SD of the crucial difference  $E = E_0^* - E$  (see constant A in “Supporting Information”, Algorithm 2) was calculated with  $\text{SD}_{\Delta E} = (\text{SD}_{E_0^*}^2 + \text{SD}_E^2)^{0.5}$ . The levels of significance (*t*-test) were calculated with a TI-58-59 calculator fitted with Applied Statistics Modul-2.

## Results

### Theoretical aspects

#### Precision and accuracy

Presuming that calibration and measurement are done at the same temperature, and using the same instrumentation (pH/mV meter, pipettes) and solutions, the error in the result in terms of calculated precision (SD) depends on the precision of the measured redox-potential and the volumes applied. The most relevant error results from the redox-potential, which can be measured with an imprecision of  $\pm 0.1$  mV. Calculated with error propagation, the error in the result (mol/L) was found to range from 0.1 to 0.78%. It depends mainly on the ratio  $R = c(\text{I}^-)/c(\text{I}_2)$ , so a high value (a surplus of iodide) shifts the error to the upper limit. The error originating from the imprecision in the volumes applied and the total error is listed in Table 1.

**Table 1** Calculated errors for measurement of an oxidant (for example 0.01 M CAT)

Parameter	Error in parameter	Error in result <sup>a</sup>
Volume of sample	$\pm 0.006$ mL <sup>b</sup>	$\pm 0.27\%$
Volume of TISAB	$\pm 0.006$ mL <sup>b</sup>	$\pm 0.07\%$
Volume of iodide solution	$\pm 0.002$ mL <sup>b</sup>	$\pm 0.20\%$
$E_{\text{red}}$	$\pm 0.1$ mV <sup>b</sup>	$\pm 0.1\text{--}0.78\%$
Total error of precision	$\Delta_{\text{prec}} = \sqrt{\sum \Delta_1^2} = 0.35\text{--}0.85\%$	
$E_0^*$	$\pm 0.1$ mV <sup>b</sup>	$\pm 0.1\text{--}0.78\%$
$c(\text{I}^-)$	$\pm 0.15\%$ <sup>c</sup>	$\pm 0.27\%$
Temperature	$\pm 0.1^\circ\text{C}$ <sup>c</sup>	$\pm 0.10\%$
Total error of accuracy	$\Delta_{\text{acc}} = \sqrt{\sum \Delta_1^2} = 0.31\text{--}0.83\%$	
Overall error	$\Delta_{\text{tot}} = \sqrt{(\Delta_{\text{prec}}^2 + \Delta_{\text{acc}}^2)} = 0.47\text{--}1.19\%$	

<sup>a</sup> Calculated by error propagation;

<sup>b</sup> Precision, specified by manufacturer;

<sup>c</sup> Estimated

Accuracy, on the other hand, is influenced by the exactness of both the standard value  $E_0^*$  and the concentration of the iodide solution, as well as the deviation between calibration and measuring temperature.

According to Table 1, the calculated imprecision ranges from 0.35 to 0.85%, while the inaccuracy ranges from 0.31 to 0.83%, which results in an overall error of  $\sim 0.5\text{--}1.2\%$ . However, by avoiding a surplus of iodide that is too large, for example by observing  $R = 3\text{--}8$ , the errors originating from  $E_{\text{red}}$  and  $E_0^*$  can be easily reduced to  $\pm 0.5\%$ , which renders a calculated overall error of  $< 0.8\%$ .

The calculated error for the method used for plain iodine solutions (Algorithm 2) is bigger and reaches 1.5–3.0%. The reason for this is that not two but three potentials ( $E_0^*$ ,  $E_1$ ,  $E_2$ ) are included in this case.

A special systematic error concerns differences in ionic strength (IS) between calibration and measurement for samples with high IS. Thus, samples with an IS of 0.1, 0.5 and 1.0 M cause an over-assessment of  $c(\text{Ox})$ , which, for Procedure A and 1.0 (0.1) M iodide, comes to 0.03 (0.23), 0.15 (1.0), and 0.28 (1.9) %, respectively.

Samples with high IS ( $> 0.1$  M) should therefore be diluted and/or analyzed with the strong iodide solution (1.0 M).

### Experimental aspects

#### Calibration experiments

With weighed samples of elemental iodine (calibration method *a*), the standard value was found to be  $E_0^* = 394.27 \pm 0.17$  mV ( $N=4$ ). Under the same experimental conditions (same day, same reagents), calibration with KIO<sub>3</sub> (method *c*) gave  $E_0^* = 394.33 \pm 0.13$  mV ( $N=6$ ), which demonstrates an excellent concordance ( $\tau = 0.635$ ,  $f=8$ ,  $P=0.457$ ).

#### Experiments with dilutions of 0.5 % chloramine T (CAT) down to 0.00005%

The results summarized in Table 2 show a maximum inaccuracy of  $-2.4\%$ , and an imprecision given by the coefficient of variation of 0.6–1.7%, which increased to 2.5% but only at the lowest concentration. The error

**Table 2** Measurement of dilutions of 0.5% CAT (Procedure A, five replicates)

Dilution	mol/L	Result <sup>a</sup>	Accuracy <sup>b</sup>	SD (mV)	CV <sup>c</sup> (%)
–	$1.775 \times 10^{-2}$	Calibration: $E_0^* = 391.04^d$		0.15	0.76
1:3	$5.917 \times 10^{-3}$	$5.839 \times 10^{-3,d}$	–1.3%	0.20	1.38
1:10	$1.775 \times 10^{-3}$	$1.757 \times 10^{-3,d}$	–1.0%	0.13	0.96
1:50	$3.550 \times 10^{-4}$	$3.522 \times 10^{-4,d}$	–0.8%	0.22	1.67
1:500	$8.875 \times 10^{-5}$	Calibration: $E_0^* = 389.75^e$		0.15	0.63
1:500	$3.550 \times 10^{-5}$	$3.467 \times 10^{-5,e}$	–2.4%	0.19	1.42
1:2000	$8.875 \times 10^{-6}$	$8.714 \times 10^{-6,e}$	–1.9%	0.18	1.41
1:10000	$1.775 \times 10^{-6}$	$1.773 \times 10^{-6,e}$	–0.1%	0.32	2.45

<sup>a</sup> Dilution, calculated from the result in mol/L;

<sup>b</sup> Difference between calculated and measured concentration;

<sup>c</sup> Coefficient of variation (concentration);

<sup>d</sup> Based on calibration with 0.500% CAT solution, Procedure A and TISAB I;

<sup>e</sup> Based on calibration with 0.025% CAT solution, Procedure B and TISAB III

(SD) in the underlying redox-potentials ranged from 0.13 to 0.32 mV.

#### Consistency of measurements at pH 2 and 8

A 0.5% CAT solution was measured using Procedure A with both TISAB I and TISAB IV. Calibration was performed in both cases with iodine solution. Table 3 shows that the result at pH 8 is about  $7 \times 10^{-5}$  M lower. This difference (as well as the difference  $E_0^* - E_{\text{red}}$ ) is not significant ( $\tau = 1.79$ ,  $f = 4$ ,  $P = 0.852$ ). Furthermore, though identically calibrated, the  $E_0^*$  values differ by 1.35 mV, which confirms that calibrations only apply to one and the same TISAB solution.

#### Comparison of redox-iodometry with iodometric titration

Both methods were calibrated with 3000  $\mu\text{L}$  aliquots of a  $7.500 \times 10^{-3}$  M  $\text{KIO}_3$  solution, resulting in the factor  $1.0075 \pm 0.0039$  ( $N = 7$ ) for the 0.1 M  $\text{S}_2\text{O}_3^{2-}$  solution and the standard value  $E_0^* = 390.10 \pm 0.13$  mV ( $N = 6$ ), respectively. 3000  $\mu\text{L}$  aliquots of a 0.5% CAT solution were analyzed with both methods, giving  $c(\text{Ox}) = (1.776 \pm 0.007) \times 10^{-2}$  ( $N = 6$ ) by titration, and  $c(\text{Ox}) = (1.781 \pm 0.012) \times 10^{-2}$  ( $N = 7$ ) by redox-iodometry (Procedure A), giving a difference of 0.28% which, however, was not significant ( $\tau = 0.969$ ,  $f = 11$ ,  $P = 0.647$ ).

100-fold, 1000-fold and 10,000-fold dilutions of the 0.5% CAT solution (equaling 12.6, 1.26 and 0.13 mg  $\text{Cl}_2/\text{L}$ ) were measured in the same way. As expected, the inaccuracy (deviation from calculated value,  $\Delta\%$ ) and the imprecision (coefficient of variation, CV) increased with dilution.

The  $\Delta\%$  (CV) values were +0.17 (0.90), +6.1 (4.0), and +94.5 (17.4) in the case of titration, while they were –3.7 (0.90), –9.3 (2.0) and –9.3 (6.9) with redox-iodometry. As can be seen, iodometric titration is more precise down to 100-fold dilution ( $c(\text{Ox}) = 1.775 \times 10^{-4}$  M), while redox-iodometry was clearly superior at 10,000-fold dilution.

#### Analysis of chlorine bleach

Ten-fold dilutions of a partially exhausted hypochlorite solution (initially 5% chlorine) were treated in the same way as described in the “Experimental” section. The results were:  $c(\text{Ox})_{\text{pH}2} = 0.360 \pm 0.003$  mol/L  $\text{Cl}^+$  and  $c(\text{Ox})_{\text{pH}8} = 0.351 \pm 0.003$  mol/L  $\text{Cl}^+$ , each with  $N = 3$ . The difference comes to  $\Delta c(\text{Ox}) = (9.0 \pm 4.2) \times 10^{-3}$  M ( $\tau = 3.67$ ,  $f = 4$ ,  $P = 0.979$ ), and this can be attributed to the presence of 4.5 mmol of chlorite impurity.

#### Analysis of a reducing substance

The applicability of the method was tested with weighed samples of ascorbic acid (Procedure A and calibration with iodine solution). The results, calculated with  $\Sigma = 1$ , are shown in Table 4, and reveal an inaccuracy of  $< 1\%$ .

#### Influence of sample dilution

Solutions of sodium hypochlorite ( $7.25 \times 10^{-2}$  M) and  $\text{KIO}_3$  ( $2.38 \times 10^{-3}$  M) were analyzed using Procedure A and TISAB I. 0, 1000, 2000, 2500 and 2700  $\mu\text{L}$   $\text{H}_2\text{O}$  were added to 3000, 2000, 1000, 500 and 300 mL of both samples, which corresponds to dilutions down to 1:10. Each dilution was measured three times. The means of

**Table 3** Measurement of 0.5% CAT solution at pH 2 and pH 8

	pH 2 (TISAB I)	pH 8 (TISAB IV)
Calibration <sup>a</sup>	$E_0^* = 392.62 \pm 0.058$ mV	$E_0^* = 391.62 \pm 0.058$ mV
Measurement <sup>a</sup>	$E_{\text{red}} = 326.33 \pm 0.058$ mV	$E_{\text{red}} = 325.25 \pm 0.058$ mV
$\Delta E_0^*$	$1.35 \pm 0.08$	
$E_0^* - E_{\text{red}}$	$5.94 \pm 0.08$ mV	$6.02 \pm 0.08$ mV
$c(\text{Ox})$ , mol/L	$(1.733 \pm 0.0067) \times 10^{-2}$	$(1.726 \pm 0.0067) \times 10^{-2}$
$\Delta c(\text{Ox})$	0.4%	

<sup>a</sup> Three replicates each

**Table 4** Quantitative analysis of ascorbic acid<sup>a</sup>

Sample (mg)	$E_{\text{red}}$	Result (mg)	Error ( $\Delta$ %)
5.73	325.1	5.71	-0.35
6.73	323.4	6.67	-0.89
9.86	317.2	9.77	-0.92
11.82	312.3	11.74	-0.68
13.46	306.7	13.50	+0.30

<sup>a</sup> 3000  $\mu\text{L}$  TISAB II and 1000  $\mu\text{L}$  iodine/iodide solution was added to weighed samples dissolved in 3000  $\mu\text{L}$   $\text{H}_2\text{O}$ ;  $E_0^* = 394.40 \pm 0.21$  mV ( $N=2$ )

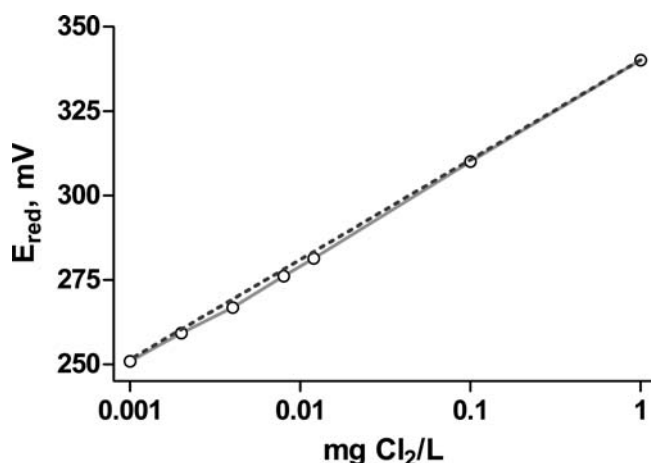
both test series were  $(7.247 \pm 0.062) \times 10^{-2}$  M for hypochlorite and  $(2.381 \pm 0.032) \times 10^{-3}$  M for  $\text{KIO}_3$ , respectively. The variation coefficients were 0.85 and 1.4%, while linear regression (result versus mL sample) gave correlation coefficients of 0.0012 and 0.1178 for hypochlorite and  $\text{KIO}_3$ , respectively. The deviations of the slopes from zero were not significant in both cases, showing an excellent robustness of the method against sample dilution.

#### Experiments with extremely low concentrations

Dilutions of a solution containing  $1.41 \times 10^{-5}$  M CAT (1 mg  $\text{Cl}_2/\text{L}$ ) were measured down to a concentration of 0.001 mg  $\text{Cl}_2/\text{L}$  using Procedure B with TISAB III. The result shown in Fig. 1 points to a fairly straight calibration curve. Linear regression resulted in a correlation coefficient  $r^2 = 0.9994$ , and the slope was  $30.01 \pm 0.34$  mV/decade (theoretical value 29.58).

#### Detection limit

For this test, the measuring system was thoroughly cleaned and the samples were aliquots of bidistilled

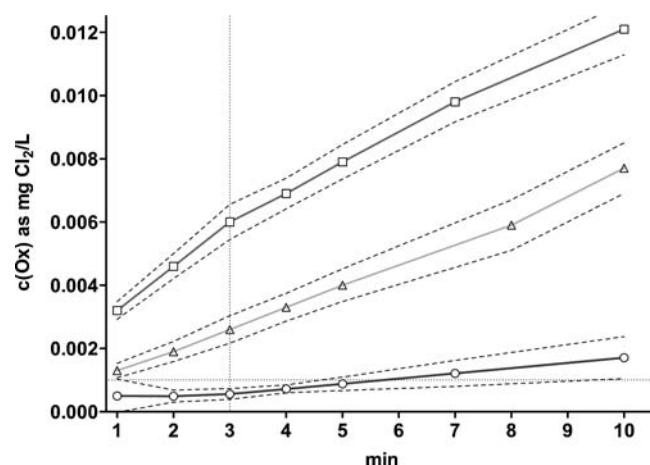


**Fig. 1** Typical calibration curve for very low concentrations; open circles indicate dilutions of  $1.41 \times 10^{-5}$  M CAT (1 mg  $\text{Cl}_2/\text{L}$ ); dotted line indicates theoretical slope (29.58 mV/decade); each point represents the mean of five independent experiments

water. Using Procedure B and TISAB III, the blank values amounted to  $c(\text{Ox}) = (7.4 \pm 0.4) \times 10^{-9}$  M. With  $\text{DL} = \text{mean}_{\text{blank}} + 3 \times \text{SD}_{\text{blank}}$ , the detection limit comes to  $\text{DL} = 8.6 \times 10^{-9}$  M, which corresponds to  $6.1 \times 10^{-4}$  mg  $\text{Cl}_2/\text{L}$ . Exploiting Fig. 2 shows that under the same conditions the emerged iodine after 3 min corresponds to  $(5.6 \pm 1.4) \times 10^{-4}$  mg  $\text{Cl}_2/\text{L}$ , resulting in a detection limit of  $\text{DL} = 9.8 \times 10^{-4}$  mg  $\text{Cl}_2/\text{L}$  and  $1.4 \times 10^{-8}$  M  $\text{Cl}^+$ , respectively. From these results, it can be deduced that redox-iodometry is well suited to concentrations down to an equivalent of 0.001 mg  $\text{Cl}_2/\text{L}$  (see also Fig. 1).

#### Testing plain iodine/iodide solutions

- Ten-fold diluted Lugol's solution: the procedure was the same as that of Procedure C with TISAB II and 0.500 M KI. The mean of three experiments was  $E_1 = 397.9 (\pm 0.0)$  and  $E_2 = 341.3 \pm 0.1$  mV. Calibration with 0.1 M iodine solution gave  $E_0^* = 394.0 \pm 0.1$  mV. The result calculated with Algorithm 2 was  $c(\text{I}_2) = (2.01 \pm 0.01) \times 10^{-2}$  M, which is 2% higher than the theoretical value ( $1.97 \times 10^{-2}$  M  $\text{I}_2$ ). This difference, however, is not significant ( $\tau = 0.069$ ;  $f = 2$ ,  $P = 0.049$ ). Iodometric titration calibrated in the same way gave  $c(\text{I}_2) = (1.958 \pm 0.005) \times 10^{-2}$  M, which is 0.6% lower. This difference, too, is not significant ( $\tau = 4.157$ ;  $f = 2$ ,  $P = 0.947$ ).
- Three-fold diluted 0.1 M iodine solution: the procedure was the same as that of Procedure C with TISAB II and 0.500 M KI, six replicates.  $E_1$  was used for the calibration with Algorithm 3, while  $E_1$  and  $E_2$  were used to calculate the concentration with Algorithm 2. Each pair of potentials was treated independently; each experiment had its own calibration. The result was  $c(\text{I}_2) = 0.1016 \pm 0.004$  M, which is



**Fig. 2** Blank tests with Procedure B at pH 2.2 (TISAB I, open squares), pH 4.5 (TISAB II, open triangles), and pH 6.6 (TISAB III, open circles); mean  $\pm$  SD (solid and dotted lines) of five repetitive measurements

1.6% greater than it should be. This difference, however, is not significant ( $\tau=0.980, f=5, P=0.628$ ).

### Comparing Algorithm 1 with Algorithm 2

An  $\sim 0.05\%$  CAT solution (Theory:  $1.775 \times 10^{-3}$  M) was treated according to Procedure A with TISAB II and 0.500 M iodide solution. After reading the redox-potential ( $E_1$ ), the addition of iodide was repeated and the redox-potential was read for a second time ( $E_2$ ).  $E_1$  was used to calculate  $c(\text{Ox})$  with Algorithm 1 while  $E_1$  and  $E_2$  were used to calculate it with Algorithm 2 ( $E_0^*=394.35$  mV, calibrated with method *b*). The result summarized in Table 5 shows that both methods agree very well, with an average difference of  $-0.48\%$  for Algorithm 2 (last row), which, however, is not significant ( $\tau=0.514, f=8, P=0.379$ ). Algorithm 2 represents, therefore, a simple control for the redox-iodometric measurement of oxidants, which, experimentally, requires only a second addition of iodide.

### Computational accuracy

The developed GWBASIC programs allowed us to calculate (iteration routine) the result with up to six digits of accuracy within less than one second. The computational accuracy was found by calculating the redox-potential of fictitious standard iodine solutions (combinations of  $c(\text{I}_2)=0.0001, 0.001$  and  $0.01$  M with  $c(\text{I}^-)=0.01, 0.1$  and  $1.0$  M) with Algorithm 3 and Eq. 18 and recalculating  $c(\text{Ox})$  of said solutions with Algorithm 1, in both cases with the same  $E_0^*$ . In all nine combinations, the difference between both the given and the calculated  $c(\text{Ox})$  values was  $<0.001\%$ . Similar procedures resulted in the same error for calculations with Algorithms 2 and 3.

## Discussion

### Disparity of redox-iodometry and iodometric titration

Besides the operational equipment, the main variations concern (a) the technique used to measure the developed iodine, and (b) fundamental features concerning precision.

- Titration deals with a steady-state reaction, while redox-iodometry is based on a real equilibrium. As a consequence, redox-iodometry has to be conducted at conditions where the complete oxidation capacity is transformed into the iodine species, which are included in the algorithms (see Eq. 4–6). This is not the case for HOI and its derivatives ( $\text{OI}^-$ ,  $\text{HI}_2\text{O}$ ,  $\text{I}_2\text{O}^-$ ). Therefore, the qualification of redox-iodometry is debatable at neutral or weak alkaline milieu. The latter, however, is necessary for preventing iodide oxidation of highly diluted samples or for discriminating analysis, for example of hypochlorite in presence of chlorite (see titration with arsenite at pH 8.3 [8]), which reacts only in an acid milieu with iodide [9] (see “Experimental”). Calculations [5] show that at the conditions of Procedure B at pH 6.6, the relative equilibrium concentration of HOI comes to  $0.014\%$  of the total oxidation capacity ( $c(\text{Ox}) \leq 1e-04$  M), while it is  $<0.05\%$  with Procedure A at pH 8.3 ( $c(\text{Ox}) \leq 0.01$  M). Because of these low errors, redox-iodometry also can be used at the quoted conditions.
- Since modern titration assemblies are able to deliver titrant volumes with an imprecision of  $\pm 0.001$  mL, the theoretical error depends on the consumed titrant volume. Taking a consumption of 2.0, 1.0, 0.1 and 0.05 mL of 0.1 M thiosulphate, the error (variation coefficient) will increase from 0.05 to 2.0%. For redox-iodometry, the crucial parameter is the redox potential, which can be measured with an imprecision of  $\pm 0.1$  mV, giving a theoretical error of 0.1–0.78% (see Table 1). However, this error is independent of the actual sample concentration.

From the above, it is apparent that the precision of iodometric titration is better at high concentrations while redox-iodometry excels at low concentrations. This was also confirmed by our experiments.

### Calibration

While the measurement signal is proportional to the logarithm of the concentration of a defined species with ion-selective electrodes (ISE), in the case of redox-iodometry it is proportional to the ratio of the concentrations of oxidizing and reducing species. For iodine/iodide solutions, the relation is specified by the Nernst equation, Eq. 17. Calculated redox potentials [5] of

**Table 5** Redox-iodometric measurement of a diluted CAT solution ( $\sim 0.05\%$ ) using Algorithms 1 and 2

Measured potentials (mV)		Result $\times 1000$ (mol/L)		Difference $\Delta$ %
$E_1$	$E_2$	Algorithm 1	Algorithm 2	
319.3	295.6	1.663	1.677	+0.84
319.4	295.6	1.675	1.664	-0.66
318.9	295.2	1.616	1.625	+0.56
319.2	295.4	1.651	1.638	-0.79
319.2	295.3	1.651	1.613	-2.3
$319.20 \pm 0.19$	$295.42 \pm 0.18$	$1.651 \pm 0.022$	$1.643 \pm 0.027$	-0.48

decimal dilutions of 0.01 M iodine at pH 4 with addition of, respectively, 0.001, 0.01 and 0.1 M iodide show an impressive influence of iodide concentration (Fig. 3). The values for, say,  $c(I_2) = 0.001$  M ( $10^{-1}$  dilution) come to 629, 539, 473 and 387 mV. Moreover, in the absence of iodide, a calibration is virtually impossible because dilution causes a change of only  $\sim 7$  mV when diluting from  $10^{-3}$  to  $10^{-6}$  M. A calibration curve, therefore, is conceivable only for a defined iodine/iodide ratio, which demands the same stoichiometric coefficients  $\Psi$  and  $\Phi$  of standard and sample.

Because the redox potentials of iodine/iodide solutions measured with the platinum electrode (the gold electrode is not suited) coincide very well with the theoretical (calculated values) down to high dilutions, the "one-point-calibration" as laid down with Algorithm 3 is completely adequate at  $c(Ox) \geq 10^{-6}$  M.

### Reaction pH

The pH selected when using one of the four TISAB solutions has a decisive effect on the rate of (a) the transformation of the oxidant to be measured into iodine (Eq. 2) and (b) the (unwanted) oxidation of iodide by the oxygen of air.

a. A range of iodometrically assessable oxidants exist, which differ in terms of the pH where a quantitative reaction takes place within reasonable time. Hypochlorite and chloramines are readily measured at  $pH < 8$ , while several *N*-chloro amides [8], chlorite [9], and iodate need an acid pH (2–3). With TISAB-I, a working pH of  $\sim 2$  is ensured, which allows us to assess virtually all oxidants with the exception of chlorate, which needs an extremely acidic milieu. Figure 4 shows the influence of pH on the

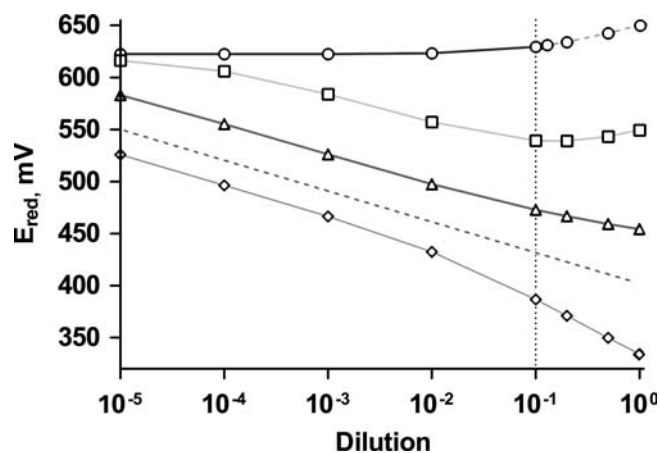


Fig. 3 Calculated redox-potentials [5] of decimal dilutions of 0.01 M  $I_2$  with addition of  $\circ$ , 0.001 ( $\square$ ), 0.01 ( $\triangle$ ), and 0.1 M KI ( $\diamond$ ) at pH 4; dotted line indicates theoretical slope (29.58 mV/decade)

equilibrium Eq. 2 in case of chloramine T, deduced from the settled redox potential. At the given iodide concentration (0.143 M) in Procedure A (with 1.0 M iodide solution), a quantitative reaction can only be expected at pH 8.4.

b. Using the half reactions  $3I^- \rightarrow I_3^- + 2e^-$  ( $E_0 = -0.5388$  V) and  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$  ( $E_0 = 1.229$  V), we can deduce that  $\Delta E = 0.6952$  V for the reaction



The equilibrium constant comes then to

$$K = \frac{[I_3^-]}{[I^-]^3 [O_2]^{0.5} [H^+]^2} = 10^{2\Delta E/0.0592} \\ = 3.19 \times 10^{23}$$

Hence, it can be inferred that the probability of iodide oxidation is very high, increasing with the third power of iodide and the second power of proton concentration. It is therefore advantageous to reduce the iodide concentration and increase the pH for the assessment of highly diluted systems. This could be confirmed by blank experiments at different pH (TISAB I, II and III) using Procedure B (see Fig. 2). In case of the iodide reagents, long-term inhibition of iodide oxidation could be attained by adjusting an alkaline milieu.

As consequences of (a) and (b), it can be deduced that extremely low concentrations of, say, residual chlorine in disinfecting systems (such as for drinking water) need a compromise between pH and iodide concentration that ensures a quantitative reaction (Eq. 2) and virtually no iodide oxidation by airborne oxygen within the measuring time of  $\sim 3$  min. This is ensured using Procedure B using TISAB III or IV.

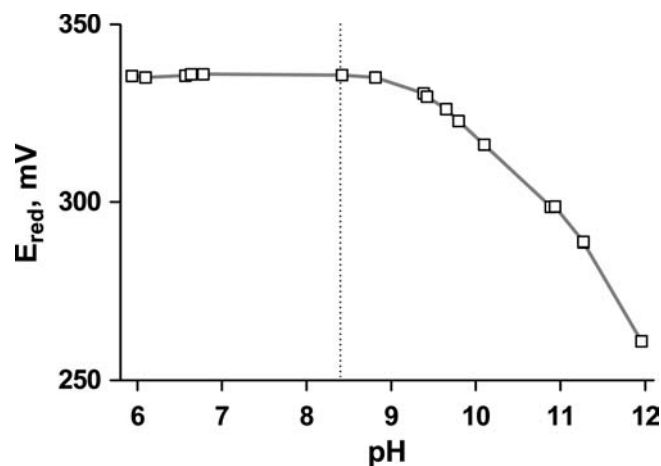


Fig. 4 Determination of the maximal pH for the quantitative reaction of  $>N-Cl$  with iodide, as measured by the redox potential. A solution of 3 mL 1% CAT and 3 mL 0.01 M citric acid was adjusted with NaOH in the pH range 6–12. After addition of 1 mL 1 M KI, equilibrium was awaited and the corresponding mV/pH pairs were read

## Concentration range

The feasible concentration range down to highly diluted systems surpasses the titrimetric procedure by two orders of magnitude. Among other factors, this is based on the sample volume needed, which can be relatively small (3–10 mL), while it has to be high (50–200 mL) for a titrimetric procedure in order to achieve an adequate sensitivity at high dilutions.

The highest concentration that can be measured with redox-iodometry depends on the concentration of the emerged molecular iodine, which is only scarcely soluble ( $[I_2] = 1.315 \times 10^{-3}$  M at 25 °C [7] in pure aqueous solution). However, the parameters chosen—the ratio of the volumes of sample, TISAB and iodide solution (and its concentration)—influence the actual concentration of  $I_2$ . Using Procedure A (1.0 M KI), the calculated maximal  $c(\text{Ox})$  comes to 0.085 M in the case of chloramine T and 0.03 M for iodate, respectively. However, these values are somewhat reduced at the high IS in the prepared measuring solution (IS 1.86 M).

The lower end, on the other hand, is delimited due to iodide oxidation via oxygen in the air. Working at pH 6.6 (Procedure B and TISAB III), this flaw can be reduced insofar as the detection limit goes down to <0.001 mg  $\text{Cl}_2/\text{L}$ . This is much better than, say, the colorimetric DPD-method, a standard in the analysis of chlorinated drinking water, for which a detection limit of 0.1 mg  $\text{Cl}_2/\text{L}$  is specified. Our own experiments with 5,5'-dithiobis(2-nitrobenzoic acid) (reduced Ellman's reagent [10]) showed a measurable concentration of ~0.05 mg  $\text{Cl}_2/\text{L}$ , while concentrations lower than 1 mg  $\text{Cl}_2/\text{L}$  were found with titration (0.1 N thiosulphate) with significant error.

## Scope of application

Redox-iodometry allows us to measure the oxidation or reduction capacity of any solution that oxidizes iodide or reduces iodine within the pH range of 2–8, and it represents an authentic counterpart to iodometric titration.

The stoichiometric coefficients  $\Phi$ ,  $\Psi$  and  $\Sigma$  enable us to also ascertain the molar concentrations of defined compounds. Moreover, plain iodine solutions can also be measured using a special algorithm. The only restriction concerns substrates containing organic polymers (such as polyvinylpyrrolidone) capable of forming complexes with iodine species. In this case, additional equilibria between the polymeric molecules (R) and the iodine species determined by Eqs. 4–6 are established, such as  $I_2 + R \leftrightarrow I_2 \cdot R$ . Since their equilibrium constants are not known [5], they cannot be reflected in the algorithms, and the calculated  $c(\text{Ox})$  would fall too short. With polyvinyl-pyrrolidone iodine [5], however, this error only appears at concentrations >0.1 g/L.

## Conclusion

The method presented marks an unparalleled approach to iodometric analysis, offering a simple, precise, cheap, and time-saving substitute for more laborious and expensive iodometric titration methods. The method presented here can be performed with ordinary equipment (electrodes, pipettes, reaction vessels, and so on) found in most analytical laboratories.

## Supporting information

*Algorithm 1:* Using the symbols  $C = c(I^-)$ ,  $E$  = measured redox-potential (potential difference of the chain platinum electrode/reference electrode), and  $E_0^*$  = standard value (see “Calibration”), the five equations 4–6, 11, and 18 with the five unknowns  $x$ ,  $y$ ,  $z$ ,  $s$ , and  $t$  can be combined to yield the polynomial Eq. 19.

$$y^2[\Phi + (\Phi + \Psi)K_3y] + y^2K_3[(2\Phi + \Psi)K_5 + 2(\Phi + \Psi)K_3K_6y]/A - \Psi A(C - y) = 0 \quad (19)$$

where  $\log A = (E_0^* - E)/S$ . The root of Eq. 19 i.e. of  $y = [I^-]$ , was found by iteration. The other components were determined using Eqs. 4–6, and 18.

The sought-after oxidation capacity of the sample solution,  $c(I_2)$ , follows from Eq. 7 while the following equation applies to the molar concentration

$$c(\text{Ox}) = c(I_2)/\Psi$$

*Algorithm 1a:* The definition of  $C$  in Algorithm 1 is changed to

$$C = c(I^-) + 2c(I_2)$$

while  $\Phi$  and  $\Psi$  are fixed at 2 and 1, respectively.

Hence, the sought-after iodine concentration according to Eq. 7 is the one that remains after the reaction,  $c(I_2)_{\text{remain}}$ .

The number of oxidized reduction equivalents equals the consumed iodine equivalents

$$c(I_2)_{\text{consumed}} = c(I_2)_{\text{init}} - c(I_2)_{\text{remain}}$$

while the molar concentration of the reducing agent amounts to

$$c(\text{Red}) = c(I_2)_{\text{consumed}}/\Sigma$$

*Algorithm 2:* With  $\log(y_i^2/x_i) = (E_0^* - E_i)/S = \log A_i$  ( $i = 1$  and  $2$ ), Eqs. 4–6 ( $i = 1$  and  $2$ ), and Eqs 16 and 17, we have ten equations for the ten unknowns  $x$ ,  $y$ ,  $z$ ,  $s$ ,  $t$  ( $i = 1$  and  $2$ ).

The two polynomials I and II for  $y_1$  and  $y_2$  below follow upon substitution:

$$\text{I. } \Omega\{y_1^2/A_1 + K_3y_1^3/A_1 + 2K_5K_3 - y_1^5/A_1^2 + 2K_6K_3^2y_1^6/A_1^2\} - y_2^2/A_2 - K_3y_2^3/A_2 - 2K_5K_3y_2^5/A_2^2 - 2K_6K_3^2y_2^6/A_2^2 = 0$$

$$\text{II. } \Omega\{y_1 + K_3 y_1^3/A_1 + K_5 K_3 y_1^5/A_1^2 + 2K_6 K_3^2 y_1^6/A_1^2\} + \Delta - y_2 - K_3 y_2^3/A_2 - K_5 K_3 y_2^5/A_2^2 - 2K_6 K_3^2 y_2^6/A_2^2 = 0$$

For a chosen value of  $y_1$ , the corresponding  $y_2$  was calculated by iteration using I. In a second iteration,  $y_1$  was modified until  $y_1$  and  $y_2$  complied with II. The other unknowns are easily calculated.

The sought-after total iodine concentration of the sample,  $c(\text{I}_2)_1$ , follows from Eq. 7.

*Algorithm 3:* The mass balances Eqs. 7 and 8 and the mass-law expressions Eq. 4–6 were transformed by substitution to the polynomial Eq. 20

$$C - xR - x^2(M - xQ - x^2N + x^3T) = 0 \quad (20)$$

where

$$C = \Psi * c(\text{Ox}), \quad D = c(\text{I}^-) - \Phi * c(\text{Ox}),$$

$$B = C - D, \quad R = 1 - BK_3, \quad T = -(K_5 K_3)^2,$$

$$M = K_3 \{2[DK_5 + B^2 K_6 K_3] + 1\} \quad (N \\ = K_3^2 [K_5^2 (2D - C) + K_5 - 2K_6])$$

$$\text{and } Q = BK_3^2 (4K_6 - K_5)$$

The root of Eq. 20 i.e.  $x = [\text{I}_2]$  was found by iteration. The second equation

$$y = [\text{I}^-] = (x - B)/(1 - K_5 K_3 x^2)$$

$y = [\text{I}^-] = (x - B)/(1 - K_5 K_3 x^2)$  is then easily solved.

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