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THE APPLICATION OF STRONGLY OXIDIZING AGENTS IN FLOW INJECTION ANALYSIS
Part 4. Manganese(VI) and Copper(III)

W.E. VAN DER LINDEN

Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede (The Netherlands)

G. DEN BOEF* and W. OZINGA

Laboratory for Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

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SUMMARY

The application of manganese(VI) and copper(III) in strongly alkaline solutions as strong oxidizing reagents in flow injection analysis is described. Both reagents were prepared under batch conditions and fed to the flow from a stock solution. The reactions of most analytes tested with manganese(VI) required the use of a heated (65°C) reaction coil. The main application appears to be for the determination of monosaccharides in the 10^{-4}-10^{-5} mol l^{-1} range.

In recent publications, the applicability of the strongly oxidizing agents silver(II), manganese(III) and cobalt(III) for flow-injection determinations of various species in acidic solutions has been demonstrated [1–3]. Although these reagents are not stable in aqueous solutions for a prolonged time, their preparation in flow, combined with their short and reproducible residence in the flow-injection device, leads to very good reproducibility of the analytical results.

In the present communication, the applicability of two reagents which can be used in strongly alkaline solutions, i.e., manganese(VI) (manganate) and copper(III), is discussed. A preparation of copper(III) in flow was possible, although very cumbersome, and that of manganese(VI) was not even attempted. Both reagents were prepared in batch and from a stock solution fed to the flow-injection device. In both cases, it was necessary to add tellurium(VI) in order to keep in solution both copper(III) and copper(II), as well as manganese(IV) formed after the reduction of manganese(VI). The stability of both reagents and the oxidizing capabilities depend on the concentration of tellurium(VI) and on the alkalinity of the solution.

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COPPER(III)

Trivalent copper has been applied in titrimetric analysis in a few cases [4–7]. In general, direct titrimetric determinations are not possible because the reactions with oxidizable compounds are too slow and the end-points of the titrations cannot easily be determined. By application of flow injection analysis (FIA), these difficulties could be overcome. The preparation of solutions of copper(III) has been known for more than a hundred years. A review of the very early work has been given by Vrtiš [8].

In the present study, copper(III) solutions were prepared by oxidizing elemental copper electrolytically in an alkaline solution containing tellurium(VI). Detection was done spectrophotometrically at 404 nm, the wavelength of maximum absorption of copper(III) in the reaction medium. It is not possible to report a reliable value of the molar absorptivity, as the concentration of the copper(III) solution cannot be precisely determined and as some concentration dependence of the absorptivity was observed. A value of about 3000 l mol^{-1} cm^{-1} may serve as an indication for the molar absorptivity. Accurate values for concentration and molar absorptivity are not required for the applications in FIA described here.

Experimental

Copper(III) solutions were prepared by electrolytic oxidation of a copper electrode with an area of 15 cm^2 during 1 h in 100 ml of solution which was 3×10^{-1} mol l^{-1} in telluric acid ($H_2TeO_4\cdot2H_2O$; BDH) and 1.4 mol l^{-1} in

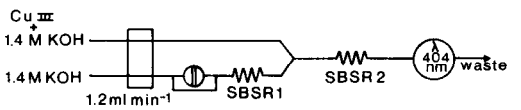

Fig. 1. Flow diagram for the determinations with copper(III). SBSR 1, 0.3 m; SBSR 2, 0.6 m; both 1-mm diameter, packed with 0.6-mm glass beads.

TABLE 1

Linear ranges for calibration curves for some analytes determined with copper(III) (1×10^{-4} mol l^{-1})

Analyte	Linear range (mol l^{-1})	Limit of determination (mol l^{-1})	Analyte	Linear range (mol l^{-1})	Limit of determination (mol l^{-1})
As(III)	2×10^{-5}-2×10^{-4}	1×10^{-5}	D(+)Glucose	2×10^{-3}-1×10^{-2}	2×10^{-3}
Sb(III)	2×10^{-5}-3×10^{-4}	1×10^{-5}	D(+)Glucose[b]	6×10^{-4}-1×10^{-2}	6×10^{-4}
Cr(III)[a]	5×10^{-4}-1×10^{-2}	3×10^{-4}	D(+)Lactose	1×10^{-3}-1×10^{-2}	1×10^{-3}
Cyanide	1×10^{-4}-1×10^{-3}	1×10^{-4}	D(+)Lactose[b]	2×10^{-4}-1×10^{-2}	2×10^{-4}
D-Fructose	2×10^{-4}-6×10^{-3}	2×10^{-4}	Saccharose[c]	—	—

[a]Deaeration of the sample solution required. [b]In these cases, a lower flow rate (0.75 ml min^{-1}) was used. [c]Very slow reaction, no determination possible.

potassium hydroxide. The potential of the copper electrode was held at 1.1 V vs. a silver/silver chloride reference electrode. A platinum wire was used as the counter electrode. In this way, a solution of about 5×10^{-3}–10^{-2} mol l^{-1} copper(III) was obtained, which could be diluted to about 10^{-4} mol l^{-1} for practical use with a solution containing the same concentrations of tellurium(VI) and potassium hydroxide as the solution in which the copper(III) had been prepared. A schematic diagram of the manifold is shown in Fig. 1. The sampling device, the pump and the detector cell were the same as described in an earlier publication [1].

Results and discussion

Copper(III) is certainly a reagent by which a number of compounds can be determined in FIA. However, when the determinations are restricted to the 10^{-4}–10^{-5} M concentration range, the number of analytes is limited. Compounds like glucose, fructose and a number of other organic compounds do react, but the reactions are too slow for application below 10^{-3} M. Manganese(VI) is more suitable for these compounds. Analytes that can be determined with copper(III) are arsenic(III), antimony(III), chromium(III) and cyanide, all in the 10^{-4}–10^{-5} mol l^{-1} concentration range. The results, together with those for some slowly reacting compounds, are summarized in Table 1. Sample solutions were prepared in 1.4 mol l^{-1} potassium hydroxide and deaerated in the case of arsenic(III) and antimony(III).

MANGANESE(VI)

It has been shown that substances like As(III), Sb(III) and Te(IV) can be determined by direct titration with manganate [9–11]. For less easily oxidizable substances, indirect titration procedures have been applied; manganate is added in excess and after a waiting time the excess is back-titrated with, for example, As(III). Such determinations could be done at temperatures up to 60 °C without appreciable decomposition of manganate [12]. Under these conditions, it was even possible to determine slowly reacting compounds like monosaccharides [13]; but about 1 hour was required to bring the reaction to completion. Because of the slowness of these processes, it was decided to examine the potentialities of manganate in FIA. Detection can be done spectrophotometrically at 605 nm, the maximum in the absorption curve of manganate ($\epsilon = 1600$ l mol^{-1} cm^{-1}).

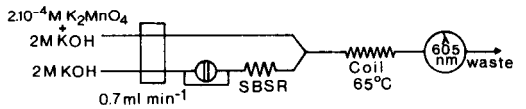

Fig. 2. Flow diagram for the determinations with manganese(VI). SBSR, 0.3 m (1-mm diameter) with 0.6-mm glass beads; coil 4.5 m, 0.75-mm diameter.

TABLE 2

Linear ranges for calibration curves for some analytes determined with manganese(VI) (2×10^{-4} mol l^{-1})

Analyte	Linear range (mol l^{-1})	Limit of determination (mol l^{-1})	Analyte	Linear range (mol l^{-1})	Limit of determination (mol l^{-1})
D-Fructose	5×10^{-5}-3×10^{-4}	3×10^{-5}	$Na_2S_2O_3$	1×10^{-3}-1×10^{-2}	1×10^{-3}
D(+)Glucose	5×10^{-5}-4×10^{-4}	4×10^{-5}	Na_2SO_3[a]	5×10^{-4}-1×10^{-3}	5×10^{-4}
L-Sorbose	5×10^{-5}-4×10^{-4}	3×10^{-5}	Cr(III)[b]	5×10^{-4}-1×10^{-2}	3×10^{-4}
D(+)Lactose	5×10^{-5}-4×10^{-4}	3×10^{-5}	Aniline	1×10^{-3}-1×10^{-2}	1×10^{-3}
Saccharose	2×10^{-4}-1×10^{-3}	2×10^{-4}			

[a]Deaeration of the sample solution required. [b]Special conditions, see text.

TABLE 3

Glucose and fructose content in lemonades

Sample	Glucose+fructose (%)		
	FIA	According to [13]	According to Schoorl-Luff [16]
7-Up	5.6±0.1	5.6±0.1	4.5±0.1
Tonic	8.7±0.2	9.0±0.1	8.5±0.1

Experimental

Potassium manganate was prepared by a procedure proposed by Jensen and Klemm [14] and further purified by following recommendations by Scholder and Waterstadt [15] (see also [9]). A 10^{-2} mol l^{-1} stock solution was prepared by dissolution of 0.2 g of potassium manganate in 100 ml of 2 mol l^{-1} potassium hydroxide containing 0.3 g of telluric acid ($H_2TeO_4\cdot2H_2O$), in order to avoid deposition of manganese dioxide formed after reduction of the manganate. Manganese dioxide formed during the preparation of the stock solution was removed by centrifugation. Manganate solutions of lower concentrations were prepared by dilution with 2 mol l^{-1} potassium hydroxide, containing the same amount of telluric acid as mentioned above.

The schematic diagram of the manifold is shown in Fig. 2. Instead of the reactor coil presented in Fig. 2, which was used in the case of slowly reacting substances, a 45-cm SBSR (single-bead-string reactor of 1 mm diameter, packed with glass beads of 0.8 mm diameter) operated at room temperature and at a 1.6 ml min^{-1} flow rate, was applied for analytes reacting more quickly, e.g., As(III) and Sb(III).

Results and discussion

Only two of the analytes tested, i.e., As(III) and Sb(III), reacted rapidly enough to allow determination at room temperature. For both analytes, the

linear range under the operating conditions (flow rate 1.6 ml min^{-1}, 45-cm SBSR, room temperature, 2×10^{-4} mol l^{-1} K_2MnO_4) was 2×10^{-5}–2×10^{-4} mol l^{-1} with a limit of determination of 1×10^{-5} mol l^{-1}.

Sample solutions as well as the potassium hydroxide solutions used for dilution were deaerated to prevent oxidation of arsenic(III) and antimony(III) by air. A sample throughput of 200 h^{-1} can be achieved under these experimental conditions.

For the other analytes, the operating conditions were: 0.7 ml min^{-1} flow rate, 4.5-m reaction coil (no packing), 65°C (thermostat), 2×10^{-4} mol l^{-1} dipotassium manganate. Useful calibration curves were obtained for sulphite, thiosulphate, aniline and a number of mono- and di-saccharides. A number of compounds tested could not be determined at sufficiently low concentration levels, mainly because of slow oxidation or no oxidation at all. These included fumaric acid, maleic acid, citric acid, tartaric acid, formic acid, aliphatic alcohols, phenol, thiocyanate and cyanide. Some ketones could be oxidized, but their determination was impossible, apparently because of the instability of these compounds in alkaline solution. The results are summarized in Table 2. All sample solutions were prepared in 2 mol l^{-1} potassium hydroxide.

Because of the low flow rate and the great length of the reaction coil, which was necessary for sufficient conversion of the analyte, considerable peak broadening occurred, resulting in relatively low sample throughputs (about 30 h^{-1}). For the monosaccharides, the reaction was fast enough for the flow rate to be increased to 1.6 ml min^{-1} and for a coiled 1-m SBSR to be used instead of the 4.5-m reaction coil; the sample throughput was then about 150 h^{-1}.

Chromium(III) is very quickly oxidized by atmospheric oxygen in alkaline solution. Therefore, the sample solutions had to be deaerated and the experimental conditions had to be adapted to decrease the residence time (coiled 1-m SBSR with glass beads, flow rate 1.6 ml min^{-1}). Furthermore, a 10^{-3} mol l^{-1} solution of manganate was used for this analyte.

The method was also applied to the determination of the total glucose and fructose content of some lemonades, which is possible because the reaction rate of these two monosaccharides with manganese(VI) is exactly the same and the disaccharide, saccharose (sucrose) hardly contributes to the total signal. The results (Table 3) are in good agreement with those obtained by other methods.

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