Exploiting a Micellar Medium in Flow Injection Analysis: Spectrophotometric Determination of Copper in Fungicides and Fertilisers

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Abstract

The combination micellar media/flow analysis was exploited to improve the spectrophotometric procedure for copper determination based on the reaction of Cu^{2+} with diethyldithiocarbamate. Effects of different micellar media established after addition of the surfactants SDS, CTAB, Triton X-100, Brij-35 and Tween-80 were studied. With Triton X-100, a remarkable improvement in the determination was verified, and a 4-fold expansion in dynamic range was attained without modifying the system design. Troubles related to baseline drift were not observed and washing time as well as measurement precision were improved. As applications, fungicide and fertiliser analyses were selected.

Keywords Micellar media, flow analysis, spectrophotometry, fungicides, fertilisers, copper

1. Introduction

Micelles are dynamic aggregates presenting both hydrophilic and hydrophobic structures with spontaneous association in aqueous solution. They are formed after addition of surfactants in a concentration beyond a threshold value, namely the critical micellar concentration, CMC[1-4]. The aggregates may modify some relevant characteristics of the medium such as solubility of ions and molecules, concentrations at the equilibrium conditions, redox properties, reaction rates and chemical pathways, as well as reaction stereochemistry[5]. Addition of surfactants is then often beneficial to enhance analytical sensitivity and/or selectivity of analytical procedures.

In flow analysis, suspensions and micellar media[6,7] are efficiently managed, so that the conditions for reaction development are enhanced, thus improving the performance of analytical methods. In view of the inherent characteristics of the flow analyser, organised micellar media can be efficiently and reproducibly established after the surfactant addition[6,7]. The combination of flow analysis with micellar media is then an interesting strategy, also in relation to spectrophotometric methods (Table. 1).

The aim of this work was then to exploit the potentialities of this combination in order to improve the spectrophotometric determination of copper in fungicides and fertilisers based on reaction of Cu^{2+} with diethyldithiocarbamate (DDTC). The potentialities and limitations of the strategy are discussed. For comparative purposes, a kinetic method for cobalt determination based on the catalytic effect of Co^{2+} in the Tiron oxidation by hydrogen peroxide in micellar media was also outlined.

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Table 1. Micellar media in association with spectrophotometric flow analysis

Surfactant	Remarks	Ref.
CTAB	Reaction rates determined for the catalysed hydrolysis of acetyl-salicylic acid in aqueous, micellar or microemulsion medium	8
SDS	A fast and efficient method for determining CMC by monitoring the change of a physicochemical property of the solution with increasing surfactant concentration	9
CPC	Determination of sulphite and formaldehyde with 5,5'-dithiobis(2-nitrobenzoic acid); 100 determinations per hour	10
Triton X-100	Determination of neodymium in glasses with 1-(2-pyridylazo)-2-naphthol; 120 determinations per hour	11
SDS	Determination of arylamines and sulphonamides by diazotization and coupling reactions	12
CTAB	Determination of hydrazines, hydrazides, amines and amino acids, based on micellar-catalysed reaction with 1-fluoro-2,4-dinitrobenzene; 40 measurements per hour	13
Triton X-100	Determination of gadolinium with 1-(2-pyridylazo)-2-naphthol	14
CTAB	Determination of sulphite with 5,5'-dithiobis(2-nitrobenzoic acid), exploiting gas diffusion and micellar catalysis	15
CPC, CTAB, Triton X-100, SDS, Nemol	Use of surfactants to improve the determination of organic species; emphasis to their effects on chromogenic derivatization reactions	16
SDS	Determination of nicotinic acid in pharmaceuticals based on König reaction	17
CTAB	Determination of cyanide in organic samples from industrial processes using the pyridine-barbituric acid reagents	18

CPC = Cetylpyridinium chloride; Nemol = Nemol K1030 = Ethylene oxide condensate.

2. Experimental

2.1. Reagents

All reagents were prepared with analytical grade chemicals and freshly de-ionised water.

A 1000.0 mg l^{-1} Cu stock solution was prepared by dissolving 0.9558 g $Cu(NO_3)_2 \cdot 5H_2O$ in water, adding 10 ml of 9.0 mol l^{-1} H_2SO_4 and diluting to 250 ml with water. Working standard solutions were prepared in 0.1 % (v/v) HNO_3 and covered the 0.0 – 30.0 mg l^{-1} Cu range. The 0.5 mol l^{-1} borate buffer solution (R_1 - Fig. 1) was based on boric acid and the pH was adjusted to 9.0 with 5.0 mol l^{-1} NaOH. The colour forming reagent (R_2) was a 0.5 % (w/v) sodium diethyldithiocarbamate, DDTC, plus 0.5 % (w/v) Triton X-100 solution. The sample carrier stream (C) was a 0.1 % (v/v) HNO_3 solution.

The Mn, Mg, Ca, Fe, Co (as nitrate salts) and Ni (based on metallic powder) solutions used for selectivity evaluation were prepared in 0.1 % (v/v) HNO_3 and the surfactants Triton X-100, polyoxyethylene 9,5-t-octylphenol, nonionic; CTAB, cetyltrimethylammonium bromide, cationic; Tween-80, polyoxyethylene sorbitan monooleate, neutral; SDS, sodium dodecylsulphate, anionic and Brij-35®, polioxyethylene dodecanol, nonionic were used in different concentrations.

2.2. Apparatus

An IPC-08 Ismatec peristaltic pump with Tygon pumping tubes was used. A model 432 Femto spectrophotometer with an U-shaped tubular flow cell (18-mm optical path, 120-µl illuminated volume) was coupled to a Kipp & Zonen strip-chart recorder. A three-piece injector made in metacrylate[19], polyethylene tubing of the non-collapsible wall type (i.d. 0.8 mm), metacrylate connectors and other common accessories were used to built-up the flow systems.

For accuracy assessment, a model AAnalyst 300 (Perkin-Elmer, Norwalk, CT, USA) atomic absorption spectrometer equipped with a background

corrector system based on a deuterium lamp was used. The system was operated according to the manufacturer recommendations for maximal sensitivity with air-acetylene flame: wavelength = 324.8 nm, slit = 0.7 nm, air flow rate = 10.0 l min^{-1}, acetylene flow rate = 2.0 l min^{-1}, analytical range = 1.0 - 4.0 mg l^{-1} Cu.

2.3. The flow system

The flow set up for spectrophotometric determination of copper (Fig. 1) was dimensioned according to that described by Blanco et al[20] who exploited the Cu-DDTC reaction in a flow system.

The step of liquid-liquid extraction in CCl_4 was not needed. After selected, the 80-μl sample volume was introduced into the carrier stream and transported towards detection. The mixed buffer and colour-forming reagent stream merged at the following confluence point, allowing the main reactions to proceed downstream, inside the reactor B. Thereafter, the processed sample passed through the flow cell and the resulting recorded peak was proportional to the copper concentration in the sample. In the present procedure, peak height constituted the measurement basis.
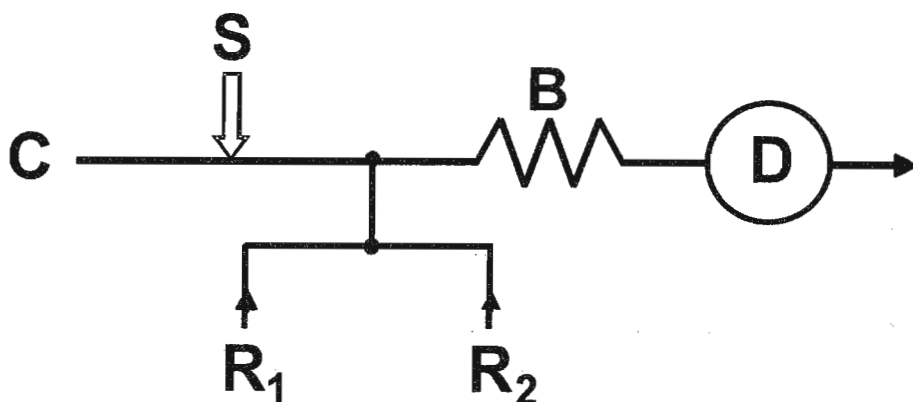

Fig. 1. Flow diagram. S = sample (80 μl); C = carrier stream (0.1 % HNO_3, 3.4 ml min^{-1}); R$_1$ = borate buffer (0.5 mol l^{-1}, pH 9.0, 1.8 ml min^{-1}); R$_2$ = colour-forming reagent (0.5 % DDTC + 0.5 % Triton X-100, 0.5 ml min^{-1}); B = reaction coil (330 cm); D = detector (452 nm).

2.4. Procedure

For optimising the copper determination, some conditions for Cu-DDTC complex formation were investigated with the flow system in Fig. 1, into which 0.5 - 30.0 mg l^{-1} Cu standard solutions were injected in triplicate. Optimisation was based on the one-parameter-at-a-time approach, and the main investigated parameters were: wavelength (400 - 500 nm), sample injected volume (ca 50 -1500 μl, 10 - 300 cm sampling loop), reactor length (160 – 700 cm), DDTC concentration (0.0005 – 1.0 % w/v), reaction pH (5 - 9), carrier stream flow rate (1.8 – 3.6 ml min^{-1}), and surfactant concentration (0.0 – 1.0 %

w/v). A factorial design[21] requiring nine experiments with three levels and two variables was performed for pH and wavelength optimisation. For accuracy assessment, liquid and solid samples prepared in 0.1 % (v/v) HNO_3 were run by the proposed method and by flame atomic absorption spectrometry. Furthermore, the main analytical characteristics of the system were evaluated and the system was applied to the analyses of fungicides and fertilisers.

The strategy involving the establishment of micellar media was also applied to a kinetic procedure carried in a similar manifold. The spectrophotometric catalytic determination of cobalt based on Tiron oxidation by hydrogen peroxide[22]

was selected and different organised media were similarly exploited.

3. Results and Discussion

Influence of the main parameters involved in the determination of copper and thus system dimensioning were similar to that previously indicated[20].

After adding the surfactants Brij-35, Tween-80, SDS, CTAB, Triton X-100 at different concentrations (0.0 - 1.0 % w/v), it was verified that the establishment of micellar media always modified the DDTC-Cu reaction. A noteworthy feature was the expansion of analytical range for all the tested surfactants, that resulted in linearization of the analytical curve (Fig. 2). In fact, the increase in analytical signals associated with the upper standard solutions minimised the curve bending.
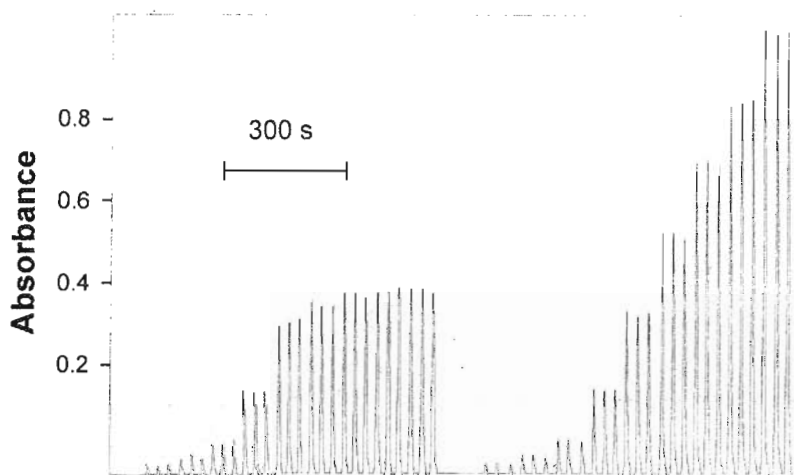

Fig. 2. Recorder output related to copper determination. Signals in triplicate refer to 0.50, 1.00, 2.00, 5.00, 10.0, 15.0, 20.0, 25.0 and 30.0 mg l^{-1} Cu in absence (left) and in the presence (right) of 0.5 % w/v Triton X-100.

Peak heights recorded for 25.0 mg l^{-1} Cu increased (18 - 107 %) under micellar media (Table 2). The increments observed in relation to Brij-35, Tween-80 and CTAB were less pronounced, although enhancements of up to 80% were attained. For SDS and Triton X-100, similar results were obtained and the increase in analytical signal reached 107%. Regarding surfactant concentration, a similar tendency was observed for most of the tested conditions emphasising that, although CMC was surpassed, the number of aggregates could be a limiting factor. Triton X-100 (0.5 % w/v) was then elected for further experiments.

Increasing the DDTC concentration up to 0.1% (w/v) improved the analytical sensitivity but the increase within the 0.1 - 1.0 % (w/v) range did not lead to any further increase in sensitivity. This result demonstrates that 0.5 % (w/v) DDTC corresponded already to a reagent excess. As the analytical signal for the higher standard solutions increased with the surfactant concentration, and the DDTC amount was

in excess, one can conclude that the main factor altering the analytical signal was associated to the number of micellar aggregates. Similar tendency was observed without surfactant addition, emphasising the beneficial effect of the establishment of the aggregates on which the light-absorbing species are rearranged. The loss in linearity is not associated to limitations in reagent concentration.

After defining the surfactant, the flow parameters were re-investigated and the length of the sampling loop was defined as 15 cm that means an injected volume of ca 80 µl. A situation of high sample dispersion, compatible with the expected copper contents in the assayed samples, was attained. Sensitivity could be improved simply by increasing the injected volume. Regarding this point, it should be noted that higher absorbance value (> 1.5 A.U.) was recorded for the 30.0 mg l^{-1} Cu when the dispersion coefficient was reduced to 1.5. The reaction coil length, buffer concentrations and

DDTC concentrations were defined as 330 cm, 0.5 mol l^{-1} and 0.5% (w/v), respectively.

Table 2. Influence of surfactant concentration in the determination of 25.0 mg l^{-1} Cu. Data refer to the system in Fig. 1.

Surfactant	Concentration (% w/v)	RSD (%)	Increase in analytical signal (%)
	0	1.0	-
	0.05	1.0	18
Brij-35	0.25	0.8	75
	0.56	0.6	75
	1.01	0.1	75
	0	1.0	-
	0.01	0.1	97
SDS	0.06	1.0	96
	0.24	0.7	100
	0.89	0.1	101
	0	1.0	-
	0.09	0.5	84
Tween – 80	0.30	0.1	79
	0.56	0.1	81
	1.06	0.2	78
	0	1.0	-
CTAB	0.10	0.3	78
	0.22	1.0	86
	0.44	0.1	82
	0	2.0	-
	0.20	0.1	104
Triton X-100	0.50	0.3	106
	0.80	0.1	107
	1.00	0.1	107

Wavelength was optimised as 452 nm, and pH of the reaction medium was not an important parameter, being selected as 9.0, the same value as in earlier work[20]. A complementary study was carried out to investigate the influence of EDTA addition to the borate buffer, and no adverse result was noted.

After system dimensioning, the analytical signals obtained with and without Triton X-100 addition were compared (Fig. 2). It is important to stress that with the addition of this surfactant plus DDTC, both at 0.5% (w/v), a wider copper concentration range (0.5 - 30.0 mg l^{-1}) for the determination was established.

Regarding selectivity, no interference from manganese and magnesium was noted even for 1000

mg l^{-1}. Cobalt, iron, nickel and calcium manifested themselves as potential interfering species when in concentrations higher then 2.5, 40, 20 and 400 mg l^{-1}, respectively. The criterion for defining the concentration beyond that a concomitant metal is a potential interfering agent was a deviation of ± 10 % in the analytical signal related to 5.0 mg l^{-1} Cu. These concentrations are well above those expected for the digests, considering the typical concentrations in the samples and the procedure for sample mineralisation. The proposed procedure can then be applied to routine analysis without restrictions.

4. Applications

Copper has been determined in fertiliser and fungicide samples, and no baseline drift has been observed during extended (4-h) operation periods. Precise results (RSD < 1.5 %, n = 7) are observed for samples with > 2 mg l^{-1} Cu. About 150 samples are run per hour and only 3.6 mg DDTC are consumed per determination. Detection and quantification limits were estimated as 0.3 and 0.4 mg l^{-1} Cu (n = 10), respectively. Accuracy was confirmed after running some samples already assayed by an alternative method (Table 3): after applying the t-test, no differences at the 95 % confidence level were found.

Table 3. Analyses of fertilisers and fungicides by the proposed method and by FAAS. Data expressed in % Cu (w/v), except for sample #1 (mg l^{-1} Cu); 1, 4 and 5 = liquid samples, others = solid samples; number of replications = 6.

Sample	Proposed method	FAAS
1	28.0 ± 3.0	24.0 ± 1.0
2	13.7 ± 0.6	14.0 ± 0.6
3	30.6 ± 0.9	33.0 ± 1.2
4	0.9 ± 0.1	0.9 ± 0.1
5	12.1 ± 0.4	13.2 ± 0.8

5. Conclusions

The combination micellar medium / flow analysis results in a beneficial enhancement in widening the linear dynamic range for the spectrophotometric procedure, the effect being associated to the increased local concentrations in the organised medium. Moreover, the presence of the surfactant in the reaction medium constitutes in an important way

to minimise the adherence of chemical species on the tubing inner walls of the manifold, as well as to improve the mixing conditions. This leads to an improvement in baseline stability and a lessening in carryover effects.

For the method involving Cu-DDTC reaction, a 100% enhancement in analytical signal for the higher standards was observed, leading to an expansion of the linear dynamic range. Prior steps such as the cumbersome dilutions inherent to procedures characterised by narrow linear ranges were then avoided. The strategy was also applied to flow-injection system for catalytic determination of cobalt[22]. Best results were achieved for the non-ionic Triton X-100 as compared with those above already mentioned surfactants. A 18 % increase in sensitivity was noted and the rate of the uncatalised reaction development was not modified. The sensitivity improvement was not dependent on the surfactant concentration within the 2.0 - 8.0 % (w/v) range. This result demonstrated the feasibility of organised micellar media also in relation with kinetic analytical procedures.

In summary, the beneficial synergistic effects resulting from the implementation of micellar media in flow analysis are attained and follows the tendency towards a "green chemistry". In fact, the reagent concentrations can be lessened and only "clean" surfactants, like bio-degradable detergents, are to be used.

Acknowledgements

References

[1] E. Pramauro and E. Pelizzetti, "Surfactants in analytical chemistry - Applications of organised amphiphilic media", Elsevier, New York, 1996.

[2] M.R. Porter, "Recent developments in the analysis of surfactants. Critical reports on applied chemistry", Elsevier Science Ltd., New York, 1991.

[3] D. Sicilia, S. Rubio, D. Perez-Bendito, N. Maniasso and E.A.G. Zagatto, *Analyst*, **124**, 615 (1999).

[4] M.E.F. Laespada, J.L.P. Pavón and B.M. Cordero, *Analyst*, **118**, 209 (1993).

[5] W.L. Hinze, "Solution chemistry of surfactants", Plenum Press, New York, 1979.

[6] N. Teshima and T. Sakai, *J. Flow Injection Anal.*, **16**, 275 (1999).

[7] M. Valcárcel and M.D. Luque de Castro, "Flow injection analysis, principles and applications", Ellis Horwood, Chichester, UK, 1987.

[8] S.H. Brooks, R.N. Williams and J.G. Dorsey, *Anal. Lett.*, **21**, 583 (1988).

[9] A. Berthod, S. H. Brooks and J.G. Dorsey, *J. Colloid Interface Sci.*, **122**, 514 (1988).

[10] M.S. Abdel-Latif and G.G. Guilbault, *Anal. Lett.*, **22**, 1355 (1989).

[11] J.L.P. Pavón, B.M. Cordero, J.H. Mendez and J.C. Miralles, *Analyst*, **114**, 849 (1989).

[12] J.S.E. Romero, G.R. Ramos, R.F. Coll and V.C. Martin, *Anal. Chim. Acta*, **242**, 14 (1991).

[13] C.A. Georgiou, M.A. Koupparis and T.P. Hadjiioannou, *Talanta*, **38**, 689 (1991).

[14] J.L.P. Pavón and B.M. Cordero, *Analyst*, **117**, 215 (1992).

[15] A.M.G. Prieto, J.L.P. Pavón and B.M. Cordero, *Analyst*, **119**, 2447 (1994).

[16] J.S.E. Romero, E.F.S. Alfons, M.C.G. Alvarez-Coque and G.R. Ramos, *Trends Anal. Chem*, **14**, 29 (1995).

[17] J.S.E. Romero, L. Monferrerpons, G.R. Ramos and M.C.G. Alvarez-Coque, *Talanta*, **42**, 737 (1995).

[18] J.O. Egekeze, T.M. Dowling, N. Grinberg, H.J. Perpall and G.R. Bicker, *Talanta*, **44**, 1203 (1997).

[19] H. Bergamin-Filho, B.F. Reis, A.O. Jacintho and E.A.G. Zagatto, *Anal. Chim. Acta*, **117**, 81 (1980).

[20] T. Blanco, N. Maniasso, M.F. Gine and A.O. Jacintho, *Analyst*, **123**, 191 (1998).

[21] G.E.P. Box, W.G. Hunter and J.S. Hunter, "Statistics for experiments. An introduction to design, data analysis and model building", Wiley, New York, 1978.

[22] M.A.Z. Arruda, E.A.G. Zagatto, A. O. Jacintho and S.M.B. Brienza, *J. Braz. Chem. Soc.*, **2**, 47 (1991).