ELSEVIER

Journal of Pharmaceutical and Biomedical Analysis
14 (1996) 967–975

JOURNAL OF
PHARMACEUTICAL
AND BIOMEDICAL
ANALYSIS

Fluorimetric determination of tin and organotin compounds in hydroorganic and micellar media in the presence of 8-hydroxyquinoline-5-sulfonic acid[1]

G. Jourquin[a], M.C. Mahedero[b], S. Paredes[a], J.-C. Vire[a], J.-M. Kauffmann[a,*]

[a]*Institut de pharmacie, Université Libre de Bruxelles, Campus plaine CP 205/6, 1050 Bruxelles, Belgium*
[b]*Dept Quimica Analitica, Universidad de Extremadura, Badajoz, Spain*

Received for review 15 September 1995; revised manuscript received 31 January 1996

Abstract

The fluorescence of tin(IV) complexed by 8-hydroxyquinoline-5-sulfonic acid (8-HQSA) has been studied in both aqueous and hydroorganic (acetate buffer and dimethylsulfoxide) media. Several experimental parameters such as pH, DMSO/water ratio and reactant concentration have been investigated to increase the fluorescence of the tin(IV)–8-HQSA complex. A linear relationship between tin(IV) concentration and fluorescence intensity was observed between 1.7 and 20 μM (DL = 0.7 μM). Mechanistic and quantitative studies in the presence of surfactants have been performed. Judiciously selected micellar media permitted solubilisation and quantitation of tin(IV) as well as dibutyltin compounds. A linear relationship between concentration and fluorescence intensity was found for mono-, di- and tributyltin with detection limits of 0.1 μM, 0.7 μM and 1 μM, respectively.

Keywords: Fluorimetry; 8-Hydroxyquinoline sulfonic acid; Micelles; Organotin derivatives; Tin

1. Introduction

Tin(IV) is still extensively employed in several countries for manufacturing organotin compounds which are used as antifoulant biocids (mainly tributyltin (TBT)) and as thermic stabilizers for polyvinylchloride. Recently, organotin compounds have been a matter of great concern owing to their toxic impact on the aqueous environment [1,2], and tin-containing antifoulants have been banned in the U.S. and in Japan [3]. Tin(IV) is also employed in the glass industry and in the electrocoating of tin alloys. In nuclear medicine, tin(II) served in the preparation of radiopharmaceuticals for the reduction of pertechnetate ($^{99}TcO_4^-$) to initiate complexation [4,5]. It is also used as an antioxidant in soft drinks. In pharmaceutical formulations, tin(II) fluoride is incorporated as a preservative in toothpastes. Owing to the ubiquity and toxicity of tin compounds, numerous studies have been devoted to their analysis such as, spectrophotometry of complexes of tin and of a chromophoric agent after its reduc-

* Corresponding author.

[1] Presented at the Fifth International Symposium on Drug Analysis, September 1995, Leuven, Belgium.

PII S0731-7085(96)01795-5

tion by tin(II) [6–9], and atomic absorption after extraction of the organotins from the sample matrix [10–15]. Electrochemical methods such as voltammetry [16–20], titrimetry [4,21] polarography [22–24] were developed as well, thanks to the electroactivity of Sn(II) ($E°$Sn(II)/Sn(IV) = +0.15V vs. N.H.E.). Recently, we have shown that tin(II) is readily determined in the presence of tin(IV) by oxidation at solid electrodes of the tin(II) dioxinate complex [25,26]. The reaction of tin(II) and tin(IV) with 8-HQSA was already investigated using fluorescence spectroscopy by Pal and Ryan [27] and Soroka and Vithanage [28] in hydroorganic DMF–water and in micellar media. The former study showed equal fluorescence intensities for tin(II) and tin(IV) complexes with 8-HQSA, while the latter pointed out that the complex tin(II)–8HQSA was not fluorescent. The present study was initiated to obtain further information on the fluorescence of tin(II) and tin(IV) compounds in the presence of 8-HQSA and to optimize their direct determination in complex samples of pharmaceutical interest. The advantage of using micellar media for tin(IV) and organotin was also pointed out. Oxine (8-hydroxyquinoleine (8-HQ)) is extensively used for the extraction and concentration of numerous metals from liquid complex matrices [29]. 8-HQ has been proposed for the fluorimetric determination of aluminium [30], aluminium–zinc alloys [31], niobium [32], gallium and indium [15]. Other fluorimetric determinations of total tin content as tin(IV) were reported using nicotinylhydrazone [33] or 2-chlorophenylfluorone [34] and for organotin using flavone derivatives [35].

2. Experimental

2.1. Apparatus

The fluorescence measurements were made using a SLM-8000C Aminco (Urbana, IL, USA) spectrofluorimeter equipped with a 450 W Xe lamp and an EMI–Thorn electron tube photomultiplier (Fairfield, NJ, USA). A 1 cm^2 quartz cell was used and the spectrofluorimeter was equipped with a quantum counter device (triangular cell filled with a 1 g l^{-1} rhodamine-B solution in ethylene glycol) to correct for the excitation spectra. The spectra were recorded on a GCS-286 AT computer with the scan 8000 C aquisition software. The pH measurements were made using a mini-870 pH meter. All reactants were of analytical grade unless otherwise stated. Methanol (Resco–Trade, Kortijk, Belgium) and dimethylsulfoxide (DMSO) (Labscan, Wauthier-Braine, Belgium) were used without further purification. The 8-HQSA was purchased from BDH Chemicals (Poole, UK). Tin(IV) chloride, dodecyl-, tetradecyl-, and cetylpyridinium bromide and chloride, and the chloride and bromide salts of cetyltrimethylammonium were obtained from Sigma (Beerse, Belgium). Mono-, dibutyl- and tributyltin were obtained from Aldrich (Beerse, Belgium) and hydrogen peroxide from UCB (Belgium). The acetate buffer (1 M, pH 4.8) was prepared by mixing solutions of 0.5 M acetic acid (Aristar, Poole, UK) and 0.5 M sodium acetate (Federa, Haren, Belgium) in bidistillated water. Phosphate buffer was rejected, because the anion competed with 8-HQSA for tin(IV) complexation [25,26]. The tin stock solutions were prepared by dissolution of tin chloride (II) or (IV) in degassed nitrogen 1 M HCl. The solutions were calibrated by iodatometry or complexometry [36]. The 8-HQSA stock solutions were prepared by dissolving 8-HQSA in bidistillated water containing 10% (v/v) 0.5 M acetate buffer. Dental gel samples were obtained from Colgate–Palmolive (Belgium). Tin peptonate samples were obtained from Therabel (Belgium).

2.2. Determination of the CMC

It is well known that light scattering rises markedly when a micellar structure is formed because of the greater diffraction of the excitation light passing through the sample [37]. The critical micellar concentration (CMC) was obtained by integrating the scattering of the sample as a function of increasing concentrations of surfactant. This procedure permitted simultaneous recording of the fluorescence of the complex and monitoring of the micellar-structure formation in the same sample.

2.3. Procedure

2.3.1. Method A

An appropriate volume of acetate buffer (1 M, pH 4.8) was added to reach a final concentration of 0.28 M, in a 25 ml calibrated flask, followed by 8-HQSA from a 1.0×10^{-2} M stock solution and Sn(IV) aliquots to reach concentrations ranging from 0.5 to 150 ng ml^{-1}. It should be noted that prior to tin(IV) and 8-HQSA addition, the solution was allowed to cool. The mixture was diluted to the 25 ml mark with bidistillated water. The fluorescence measurements were realized at 21 ± 2°C. The calibration curve was established using standard solutions of tin(IV) treated in the same manner. The instantaneous formation of the complex was observed and the optimal sequence addition order was found to be: buffer; DMSO; 8-HQSA; Sn(IV).

2.3.2. Method B

An appropriate volume of acetate buffer (1 M, pH 4.8) was added to reach a final concentration of 0.28 M in a 25 ml calibrated flask followed by 8-HQSA and tin(IV) from a 1.0×10^{-3} M stock solution. After addition of the surfactant, the mixture was diluted to the 25 ml mark using bistilled water.

2.4. Assay of raw material and pharmaceutical formulations

Tin peptonate samples (30 mg) were dissolved in sulfuric acid 30% (v/v) by mixing well for 10 min. Aliquots of 60 μl were spiked into a 25 ml flask and the procedure of method A was followed. Dental gel samples were dissolved by gentle stirring in the presence of 5 ml nitrogen-purged 1 M HCl and maintained at 40°C for 10 min. Aliquots of 50 μl were spiked into a 25 ml flask and method B was followed.

3. Results and discussion

3.1. Spectral characteristics

As illustrated in Fig. 1, 8-HQSA showed a weak fluorescence in acetate buffer (Fig. 1, curve (b)) which was considerably enhanced in the presence of tin(IV) (Fig. 1, curve (a.2)). However, tin(II) did not generate a fluorescent complex in the presence of 8-HQSA in contrast to the results obtained by Pal and Ryan [27] but in good agreement with those reported more recently by Soroka and Vithanage [28]. It should also be pointed out that 8-HQ complexes of Sn(II) and Sn(IV) were not fluorescent. It is well known that the fluorescence of metallic complexes may be enhanced in the presence of organic solvents such as DMF or DMSO [27,28]. The addition of DMSO increased the fluorescence of the Sn(IV)–8HQSA complex and a small shift in the wavelength of the emission maximum from 527 to 522 nm was observed. However, the excitation maximum remained at 372 nm. The amount of DMSO (corrected for pH variation) had little influence on the native fluorescence of 8-HQSA, thus, its presence in the analytical sample raised the sensitivity of the method. The relationship between the fluorescence intensity of the complex and the amount of added DMSO was found to be linear up to 40% (v/v) added DMSO.

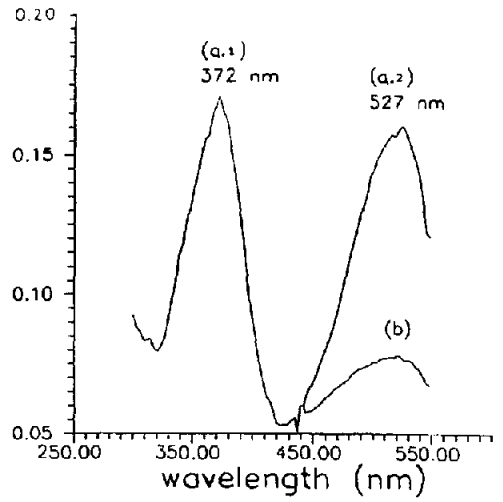

Fig. 1. Excitation ($E_m = 527$ nm) (curve a.1) and emission ($E_x = 372$ nm) spectra of Sn(IV)–8-HQSA (curve a.2) and emission spectrum of 8-HQSA ($E_x = 372$ nm) (curve b).

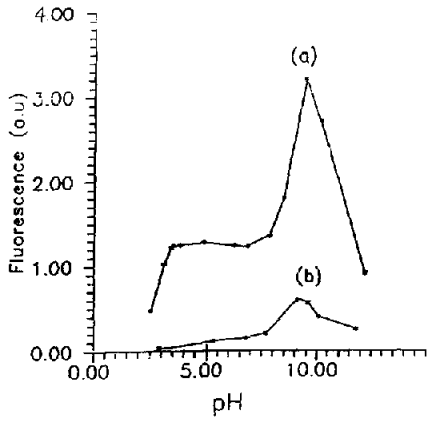

Fig. 2. Influence of pH on the fluorescence of the complex Sn(IV)–8-HQSA (a) and 8-HQSA blank (b). The excitation and emission wavelengths were 372 nm and 527 nm. The slit width was 4 nm for both excitation and emission.

The pH corresponding to maximum fluorescence of the complex (1×10^{-5} M) was investigated in 4 M NaCl (to avoid variation of ionic strength) by adjusting the pH with hydrochloric acid and sodium hydroxide solutions (2 M).

As shown in Fig. 2, the fluorescence intensity of the tin(IV)–8HQSA complex was constant between approximately pH 4 and 6. Below pH 4, the formation of the complex was not observed. The fluorescence increased sharply till the pK_{a_2} of the phenol function of 8-HQSA ($pK_{a_1} = 4.05$; $pK_{a_2} = 8.42$) [38]. Despite the high fluorescence in alkaline media, basic pH values were not selected because of the high sensitivity of the response to small pH fluctuations. The rapid decline of the fluorescence above pH 9.6 might be due to the formation of stable stannate complexes [25,26]. We may also note that 8-HQSA was slightly fluorescent up to pH 8 with a small increase of the fluorescence intensity between pH 8 and pH 10.

The influence of 8-HQSA was studied by varying its concentration from 0 to 300 μM and by keeping tin(IV) at 4.8×10^{-6} M. The fluorescence intensity increased linearly by raising 8-HQSA until 4 μM and it levelled off at higher concentrations. The stoichiometry of the complex was obtained by the molar-ratio method using fluorescence spectroscopy and spectrophotometry. In hydroorganic media (40% DMSO), for a fixed concentration of Sn(IV) (5.10^{-6} M), a 1:1 tin(IV): 8-HQSA complex was obtained initially. Subsequently, by raising the concentation of 8-HQSA till 2.0×10^{-5} M, a 1:4 complex was formed. Intermediate stoichiometries were not observed. In aqueous and micellar media, the early formation of a 1:1 complex was also observed by spectrophotometry and fluorimetry.

3.2. Temperature and stability

The fluorescence signal was stable in the investigated solutions for at least 3 h at 20°C and its magnitude was not significantly affected by varying the temperature between 20 and 30°C.

3.3. Calibration curve in DMSO

A linear relationship between the fluorescence intensity and Sn(IV) concentration was obtained in acetate buffer DMSO 40% (v/v) (pH $\approx$ 5.2) in the concentration range between 1.7 μM and 20 μM—the calibration curve ($E_x = 372$ nm; $E_m = 521$ nm) was $I_f = 0.0685C - 0.035$ with C expressed in mol l^{-1}. The correlation coefficient was 0.997. The detection ($S/N = 3$) and determination ($S/N = 10$) limits calculated following the IUPAC regulations [40] were 0.7 μM and 1.7 μM, respectively. The repeatability of the method estimated with a tin(IV) concentration of 3 μM ($n = 6$), was characterized by an RSD of 4%. The reproducibility calculated over a 10-day period with daily renewed reactants gave an RSD of 7% for a tin(IV) concentration of 1.5 μM and 4% for a concentration of 5 μM. The method was applied to the determination of total tin content as tin(IV) in a tin peptonate sample. The latter is a raw material used at lower concentrations in drug formulations for the treatment of various skin deseases. As shown in Table 1, there is a good correlation between fluorimetry and complexometry and the results are in agreement with the stated value. It should be noted that the poor precision of complexometry can be attributed to difficulties in visually determining the end-point detection.

3.4. Micellar media

Organized media are increasingly being used in analytical chemistry and particularly in luminescence and fluorescence spectroscopy because sequestration of the analyte can often improve discrimination and detection limits. Numerous authors have reported improvements in the signal-to-noise ratio on the fluorescence of metal complexes by addition of surfactants [14,30,32,39]. Surfactants have also been reported to improve the stability of some complexes [41,42]. Surfactants form relatively well-defined structures by self association of monomers above their CMC, allowing the solubilisation of a broad variety of solutes. The spectral changes in micellar media are very similar to those obtained in hydroorganic media, showing a slight shift of the emission maximum towards shorter wavelengths. It was of interest to examine the effect of various surfactants on the fluorescence intensity of 8-HQSA–tin(IV) and to study the mechanism of signal enhancement.

As is shown in Fig. 3, the fluorescence of the complex increased markedly in the presence of cationic surfactants such as cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPYB) by varying their concentration from 10^{-6} to 10^{-2} M. Neutral surfactants such as Triton X-100 and anionic surfactants such as sodium laurylsulfate did not affect the fluorescence intensity of the complex even above their CMC. Non-micelle forming voluminous cations, such as tetraethylammonium bromide or benzyltrimethylammonium bromide, had no effect on the fluorescence intensity. These findings underline the importance of the positive charge, as well as the micelle-forming ability of the surfactant. The fluorescence enhancement may be due to electrostatic attraction between the sulfonate group of the complexing agent and the cationic head-group of the surfactant. A similar phenomenon was described for the complexation of niobium with 8-HQSA [32], however, the cationic surfactants decreased the fluorescence of the complex and enhanced its absorptivity. In our study, tin(IV)–8HQSA absorptivity decreased, but only by 10%. The absorption wavelength maximum shifted from 360 to 364 nm. The absorption maximum of 8-HQSA, located around 306 nm in aqueous media, was shifted to 309 nm in micellar media.

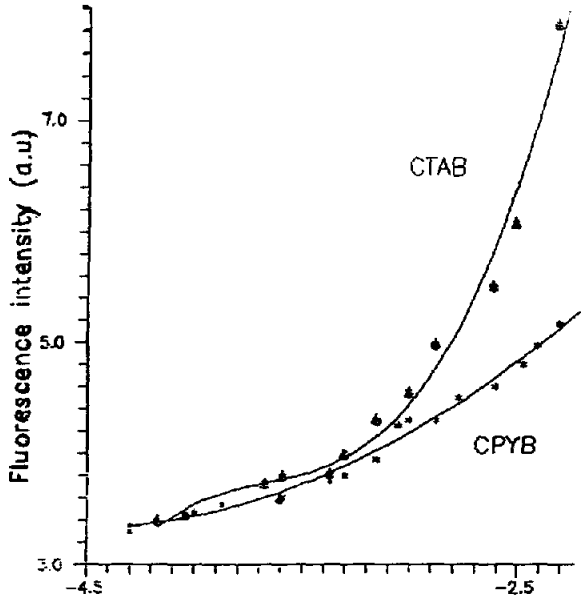

Fig. 3. Fluorescence of the Sn(IV)–8-HQSA complex (3.6×10^{-6} M) as a function of CPYB and CTAB. The excitation and emission wavelengths were 372 nm and 525 nm, respectively.

Table 1
Determination of tin content in tin peptonate (hydroorganic media)

Stated tin content (%)	Measured tin content (%) Fluorimetry	Complexometry
47	47.6	48.0
	47.1 $m = 47.7$	49.6 $m = 48.0$
	48.3 $s = 0.5$	47.3 $s = 1.5$
	47.7	45.8

From the fluorescence of the complex (Fig. 3) and by integration of the scattering, Fig. 4, we observed that the fluorescence enhancement occured at a low concentration of surfactant, i.e. 4.7×10^{-4} M and 1.27×10^{-4} M for CTAB and CPYB, respectively, and that the scattering increased at similar concentration values (within the experimental errors of the method), i.e. 6.4×10^{-4}

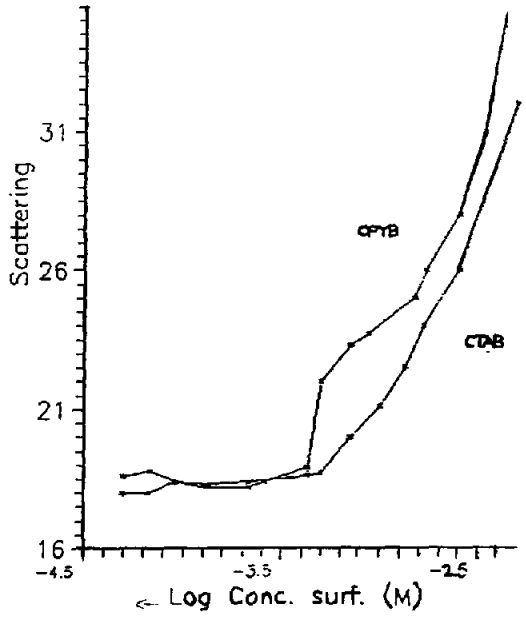

Fig. 4. Scattering of the sample as a function of CPYB and CTAB. [8-HQSA] = 4.8×10^{-5} M, Sn(IV) = 3.6×10^{-6} M. The excitation and emission wavelengths were 372 nm and 525 nm, respectively.

M and 2.28×10^{-4} M for CTAB and CPYB, respectively. The latter values correspond to the CMC of CTAB and CPYB in acetate buffer (0.28 M) in the presence of 4.8×10^{-5} M 8-HQSA and 4.8×10^{-6} M tin(IV). The micellar enhancement factor (MEF) calculated from the slope of I_f vs. log C was 1.7 ± 0.2 and 3.4 ± 0.3 for CPYB and CTAB, respectively. Actually, for a concentration of 5×10^{-3} M CTAB, a MEF of 3 was obtained. This MEF was higher than the values given by Soroka and Vithanage [28] for a series of other metal–8HQSA complexes, except for aluminium with a reported value of 10.2. The relatively large difference between the MEF of CPYB and CTAB could not be related to the small difference between their CMCs. Instead, we assume that the pyridinium chromophore of CPYB tends to lower the fluorescence efficiency of the sensitization. The amino group of the pyridinium moiety could partially deactivate the excited complex by electron transfer on the surface of the micelle [43].

3.5. Interfering species in hydroorganic and in micellar media

This study was realized by following two procedures: the interferent was added (a), to the medium containing the already formed complex, and (b), to the medium containing tin(IV) (3.6×10^{-6} M) prior to the addition of 8-HQSA. Although this latter approach yielded lower analytical tolerance, it was more realistic with regard to the analysis of unknown samples. Interferences were considered as significant when the deviation of the signal was higher than 5%. As shown in Table 2, zinc and magnesium are strong interferents. Differences between method (a) and (b) were observed for chelating species such as citrates or fluorides. We may also note that the micellar media (see below) offered a better selectivity towards ascorbic acid and Zn^{2+}.

Table 2
Effect of several interfering species on the fluorescence of Sn(IV)–8-HQSA

Interfering species	Aqueous media	Hydroorganic media	Micellar media
SO_4^-, NO_3^-, Cl^-, Br^-	> 1000:1	> 1000:1	> 1000:1
Lactose	> 1000:1	> 1000:1	> 1000:1
Ascorbic acid	10:1	10:1	100:1
Mg^{2+}	5:1	20:1	20:1
Fluoride (a)	> 50:1	> 100:1	> 100:1
Fluoride (b)	50:1	> 6:1	> 10:1
Citrate (a)	> 5:1	> 10:1	> 10:1
Citrate (b)	100:1	10:1	5:1
Zn^{2+} (a)	1:2	2:1	7:1
Zn^{2+} (b)	2:1	5:1	10:1

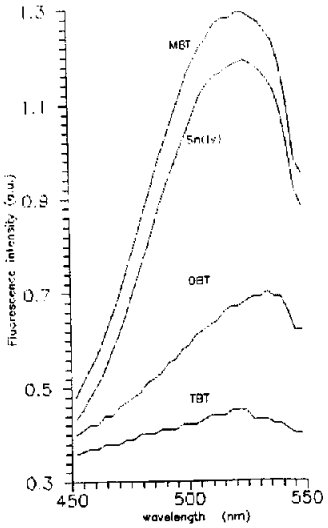

Fig. 5. Fluorescence spectra of Sn(IV), monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT); (2×10^{-5} M). E_x wavelength = 372 nm. 5×10^{-3} M CPYB.

3.6. Reactivity of mono-, di- and tributyltin

The quantitative analysis of organotin compounds is usually performed after extraction and/or preconcentration by gas chromatography–mass spectroscopy (GC–MS) [45–47] or by HPLC coupled to fluorescence detection [44,48]. Being not fluorescent per se, the organotin compounds have been labelled by post-column derivatisation using fluorescent labelling agents such as Morin [44] or flavone derivatives [35,48]. The reactivity of some organotin compounds in the presence of 8-HQSA in micellar media was studied to assess the influence of the hydrophobic core on the fluorescence of these complexes. Since organotin compounds are poorly soluble in aqueous media, this study also permitted the exploitation of the solubilisation properites of micellar assemblies. The reactivity order for the different butyltin compounds with 8-HQSA was MBT > DBT > TBT in CPYB micellar media (Fig. 5). The same order was found in methanol. We may note that Morin reagent showed higher sensitivity towards di-alkyltin compounds [44]. The detection limits (DL) were 1×10^{-7}, 7×10^{-7} and 1×10^{-6} M and the quantification limits (QL) were 1×10^{-6}, 2×10^{-6} and 6×10^{-6} M for MBT, DBT and TBT, respectively. The fluorescence intensity of inorganic tin(IV) was of the same order of magnitude than the MBT derivative.

Fluorescence spectra were recorded in micellar media (5×10^{-3} M CPYB) as a function of the surfactant chain length. No significant differences were observed for the fluorescence signal intensity of the MBT–, DBT–, and TBT–8-HQS complexes by varying the surfactant chain length, i.e. C_{12}, C_{14} and C_{16}. This tended to confirm the assumption that the complex was likely to be located near the bulk-solution interface of the micelle.

Using the same concentration range of organotin ($0–4 \times 10^{-4}$ M), in the presence of 8-HQSA and CPYB, TBT has been found to have the greatest effect on the light scattering. TBT readily produced an increase in the scattering at a concentration of 5×10^{-5} M while DBT and TBT increased the scattering at 1.4×10^{-4} M and 1.7×10^{-4} M, respectively. It was checked that the small amount of methanol present in the standard solutions of alkyltin produced no influence on the scattering. Thus, we may assume that the structure of the micelle was enhanced, or that the number of micelles in solution was increased in the presence of organotin compounds. These results suggest that the selective and sensitive

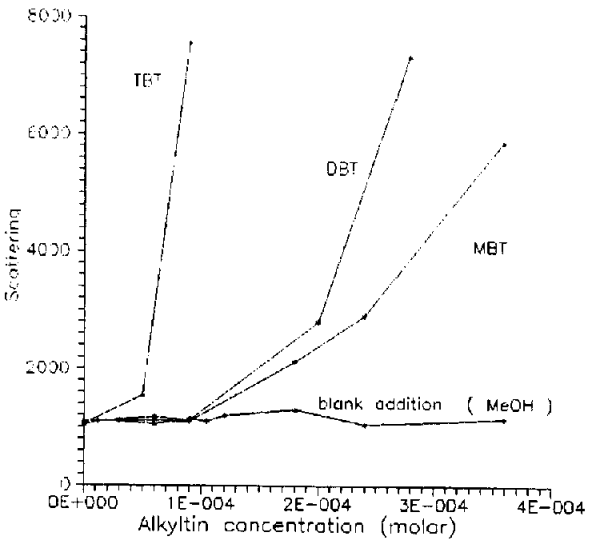

Fig. 6. Influence of TBT, DBT, TBT on scattering in acetate buffer. 5×10^{-3} M CPYB.

Table 3
Determination of tin in dental gels (Tin(II) declared = 0.4%) (micellar media)

Sample	Number of assays	Tin(IV) (% mg)	Total tin (% mg)	Tin(II)	Tin(II)
1	3	0.20	0.38	0.18	0.22
2	3	0.19	0.36	0.17	0.21

[a] Obtained by difference (total tin − tin(IV)).
[b] Obtained by iodatometry.

analysis of tin and alkyltin compounds may be performed by liquid chromatography using the above media as mobile phase with fluorescence detection [49,50].

The method was applied to the direct determination of tin(IV) and total tin in a dental gel formulation containing 0.4% (w/w) SnF_2 with hydroxyethylcellulose, glycerin and mint flavour as excipients (Table 3). Iodatometry yielded a concentration of tin(II) of 0.22% (w/w).

By applying a chemical oxidation to the sample using H_2O_2 (10 min, 40°C), tin was totally transformed into tin(IV) in 1 M HCl. Measurements were made in the presence of 5×10^{-3} M CTAB. The concentration of fluoride was too low to significantly interfere with the determination (see Table 2), also the fluoride concentration likely decreased due to fluorhydric acid volatilization. The difference between the direct measurements and those made after oxidation gave the content of tin(IV), total tin and tin(II). The amount of tin(II) obtained by iodatometry was higher by 0.04% compared to the results calculated by fluorimetry. The results in Table 3 also show that a significant amount of tin(II) was lost due to oxidation during storage of the hydrophylic gel.

4. Conclusion

The use of a DMSO aqueous media was found to be advantageous for the determination of inorganic tin(IV) in terms of sensitivity, stability and reproducibility. The complexing agent 8-HQSA appeared well suited for the fluorimetric detection of tin(IV). The mechanism of fluorescence enhancement in the presence of cationic micelles requires charged micelles, and can be explained in terms of electrostatic effects and chemical structure of the surfactant. The solubilisation properties of the micellar media allowed the successful quantitation of poorly water-soluble alkyltin compounds. Regarding the butyl substituted compounds studied, mono- and dialkyl derivatives were found to give a greater fluorescence than tributyl tin.

Acknowledgements

We are indebted to the Fonds National de la Recherche Scientifique for financial support (FRSM No. 3.4508.89)

References

[1] G. Weber, Fres. Z. Anal. Chem., 321 (1985) 217–224.
[2] H. Seiler, A. Siegel and H. Sigel, Handbook on Metals in Clinical and Analytical Chemistry, Marcel Dekker, New York, 1994.
[3] P.L. Layman, Chem. Eng. News, 73 (1995) 23–26.
[4] M. Apparecida, T. Marcillo de Almeida, C.P. Gonçalves da Silva, J. Radioanal.-Nucl. Chem. Lett., 176 (3) (1993) 225–231.
[5] O.K. Hjelstuen, Analyst, 120 (1995) 863–866.
[6] S. Bajic and B. Jaselkis, Analyst, 116 (1991) 1059–1062.
[7] V.H. Kulkarni and M.C. Good, Anal. Chem, 50 (1978) 973–975.
[8] Y.K. Agrawal, Y.K. Bhatt, V.J., Analyst, 110 (1985) 1321–1328.
[9] M. Omar and J.M. Bowen, Analyst, 107 (1982) 654–658.
[10] Z. Fang, L. Sun and E. Hansen, Talanta, 39 (4) (1992) 383–387.
[11] B. Welz, M. Schubert-Jacobs and T. Guo, Talanta, 39 (9) (1992) 1097–1105.
[12] J. Burridge and I.J. Hewitt, Analyst, 110 (1985) 795–800.
[13] L. Ebdon, S.J. Hill and P. Jones, Analyst, 110 (1985) 515–519.
[14] J. Medina Escriche, M. De La Guardia Cirugeda and F.H. Hernandez, Analyst, 108 (1983) 1386–1391.
[15] Y. Nishikawa, K. Hiraki, K. Morishige and T. Katgi, Jpn. Anal., 26 (1977) 365–370.
[16] T.V. Nghi and F. Vydra, J. Electroanal. Chem., 71 (1976) 333–340.
[17] S. Dogan, G. Nembrini and W. Haerdi, Anal. Chim. Acta, 130 (1981) 385–390.
[18] P. Kiekens, H. Verplaetse and L. De Cock, Analyst, 106 (1981) 305–310.
[19] R.V. Peddy and G. Kalpanas, Analyst, 117 (1992) 27–31.

[20] P. De Bakker, J. Vandenbalck, G.J. Patriarche and G.D. Christian, Microchem. J., 26 (1981) 92–97.
[21] W.U. Malik and M. Ajmal, J. Electroanal. Chem., 6 (1963) 450–459.
[22] S.K. Bhowal and F. Umland, Fres. Z. Anal. Chem., 285 (1977) 226–232.
[23] M. McBride and M.E. Georges, J. Pharm. Sci., 66 (1977) 870–874.
[24] J.L. Guinon and J. Garcia Anton, anal. Chim. Acta, 177 (1985) 225–229.
[25] Z.P. Yang J. Arcos, M. Alafandy, K. Boutakhrit and J.M. Kauffmann, Electroanalysis., 8 (1966) 25–29.
[26] K. Boutakhrit, Z.P. Yang and J.M. Kauffmann, Talanta, 42 (1995) 1883–1890.
[27] B.K. Pal and E.D. Ryan, Anal. Chim. Acta, 48 (1969) 227–231.
[28] K. Soroka and R.S. Vithanage, Anal. Chem., 59 (1987) 629–636.
[29] R.E. Sturgeon and S.S. Berman, Anal. Chem., 53 (1981) 2337–2340.
[30] F. Salinas, A. Munoz de la Pena and M.S. Duran, Anal. Lett., 21 (8) (1988) 1457–1468.
[31] A. Munoz de la Pena, F. Salinas and E. Sanchez, Analyst, 113 (1988) 1435–1438.
[32] J.I. Garcia-Alonso, M.E. Diaz-Garcia and A. Sanz-Medel, Talanta, 31 (1984) 361–366.
[33] S. Rubio, A. Gomez-Hens and M. Valcarcel, Analyst, 110 (1985) 43–46.
[34] J. Zhao, X. Cao, M. Guo and Y. He, Yankuang Ceshi, 8 (1989) 182–185.
[35] C. Leal, M. Granados, M.D. Prat and R. Compañó, Talanta, (1995) in press.
[36] J. Hefferren, J. Pharm. Sci., 52 (1963) 1090–1093.
[37] P. Mukerjee and K.J. Mysels, CMC of aqueous surfactant systems, NSRDS ed, 1971.
[38] R. Nasanen and A. Ekman, Acta Chem. Scand., 6 (1952) 1384–1386.
[39] M.E. Diaz Garcia and A. Sanz-Medel, Talanta, 32 (3) (1985) 189–193.
[40] IUPAC, nomenclature, symbols, units and their usage in spectrochemical analysis, Pure Appl. Chem., 52 (1976) 2242.
[41] G.L. McIntire, Crit. Rev. Anal. Chem., 21 (1990) 257–277.
[42] E. Pramauro and E. Pelizetti, Trends Anal. Chem., 7 (7) (1990) 260–265.
[43] M.F. Rodriguez Prieto, M.C. Rios Rodriguez, M.M. Gonzalez, A.M. Rios Rodriquez and J.C. Mejuto Fernandez, J. Chem. Ed., 72 (7) (1995) 662–663.
[44] Y. Arakawa and O. Wada, Anal. Chem., 55 (1983) 1901–1904.
[45] J. Szpunar-Lobinska, C. Witte, R. Lobinski and F.C. Adams, Fr. Z. Anal. Chem., 348 (1994) 1–27.
[46] J. Szpunar-Lobinska, M. Ceulemans, R. Lobinski and F.C. Adams, Anal. Chim. Acta, 278 (1993) 99–113.
[47] J. Szpunar-Lobinska, Mikrochim. Acta, 113 (1994) 287–298.
[48] C. Leal, M. Granados, M.D. Prat and R. Compañó, Talanta (1995) in press.
[49] L. Ebdon and J.I. Garcia Alonso, Analyst, 112 (1987) 1551–1554.
[50] T.H. Yu and Y. Arakawa, J. Chromatogr., 258 (1983) 189–197.