Application of a New Potentiometric Sensor for Determination of Anionic Surfactants in Wastewater

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A new *screen-printed* potentiometric microsensor (SPMS) for the determination of anionic surfactants (ASs) based on the dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion pair as a sensing material was applied to real industrial effluents. The sensor is accurate, inexpensive, simple and very sensitive. The solutions of cetylpyridinium chloride (CPC) of the concentrations down to $5 \cdot 10^{-5}$ mol dm^{-3} were used as a titrant. Standard addition method was used for checking the precision and accuracy of measurements providing satisfactory results with recoveries between 98.3 to 102.0 % in pure AS solutions and 99.0 to 114.5 % in wastewater. Standard spectrophotometric method Methylene Blue Active Substances (MBAS) was used as control for comparison of the results obtained with the new sensor. The results obtained using SPMS were compared with those obtained by the polymeric membrane ion-selective electrodes (ISEs), containing the same sensing material, and exhibited good mutual agreement.

Key words:
anionic surfactant, screen-printed, microsensor, potentiometric, wastewater

Introduction

Surfactants (surface active agents) are substances which incorporate a hydrophobic non-polar and a hydrophilic polar group, and have the tendency to accumulate at the phase boundary. This feature causes the wide application of surfactants.

In 2012, the world surfactant market amounted to 27,040 million USD, and with average annual increase of 6.18 %, this amount in 2017 is estimated at 36,518 million USD[2].

ASs are used as components in cosmetic formulations, household products, industrial cleaners. Their wide application leads to water pollution, and thus endangers the flora and fauna[3].

The standard method for the determination of anionic surfactants (ASs) in wastewater is MBAS[4] (Methylene Blue Active Substances), while two-phase titration[5] is used for determining AS in commercial products. Both standard methods have many drawbacks (use of carcinogenic organic solvents, difficulties in determination of anionic surfactants in turbid solution, the subjectivity of the person performing the analysis, inability of automation...). The limitations of the standard methods for the determination of AS impose the need for continuous development of new surfactant sensors, which are less expensive, miniaturized, easier to use.

The Environmental Protection Act of Croatia does not allow the use of surfactants whose biodegradability is less than 90 %[6], thus, the determination of low concentrations of AS in effluents is of great importance.

Today, there are a number of techniques that are able to detect, identify, and quantify the surfactant in samples of a complex matrix[7].

The first methods for determination of ASs were developed from simple volumetric methods[5], followed by spectrophotometric methods[8,9], chromatography[10–12], microfluidic techniques such as flow-injection analysis (FIA)[13], capillary electrophoresys[14], attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)[15].

The polymeric membrane ion-selective electrodes (ISEs)[16–19] successfully replace standard methods for determination of ASs in various samples. ISEs are a simpler and cost-effective alternative to standard methods. ISEs have evolved from the coated-wire electrodes and liquid polymeric membrane electrodes containing ion-pair based sensing material. The widest use have found ISEs with PVC liquid membrane.

Low concentrations of ASs can be determined by ISFET sensors[20], biosensors[21] or ISEs associated with FIA system.

The aim of this study was the application of a newly developed screen-printed microsensor, based on dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion pair as a sensing material, for determination of ASs in industrial wastewater. Particular attention was paid to the determination of low concentrations of ASs.

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Experimental

Reagents and materials

Sodium dodecylsulphate (NaDDS) and sodium dodecylbenzenesulphonate (NaDBS) (from Fluka, Switzerland) were used for the examination of the sensor response and for potentiometric titrations. The standard solution of cetylpyridinium chloride (CPC), (Merck, Germany), was used as a cationic titrant. Sodium hydroxide (T.T.T., Croatia), hydrochloric acid (Carlo Erba Reagent, Italy) were used to adjust the pH while studying the pH influence on the titration curves. Sodium sulphate (Kemika, Croatia) was used for ionic strength adjustment. The applicability of a new *screen-printed* microsensor was tested at five industrial effluent samples of different AS concentration.

For the preparation of sensor membrane dimethyldioctadecylammonium chloride (DDAC), sodium tetraphenylborate (NaTPB), *o*-nitrophenyloctylether (*o*-NPOE) and high molecular weight PVC (Fluka, Switzerland) were used.

Apparatus and measurements

An all-purpose titrator (808 Titrando) and 806 Exchange unit (both Metrohm, Switzerland) controlled by Tiamo software were used to perform the potentiometric titrations. The solutions were magnetically stirred during the titrations and measurements by an 801 Titration stand (Metrohm, Switzerland). A 780 pH meter, 728 Stirrer, 794 Basic Titrino (all Metrohm, Switzerland) and in-house software were used for the response measurements. A *screen-printed* electrode DRP-C110 (DropSens, Spain) was used for microsensor preparation.

Sensor

Ion-exchange complex DDA-TPB was used for the preparation of the PVC-based membrane plasticized with *o*-NPOE. A detailed explanation of the preparation of the DDA-TPB complex has been provided previously[22]. The *screen-printed* microsensor (SPMS) was prepared by applying 0.005 cm³ of membrane solution on the DRP-C110 electrode, and the electrode was left for 24 hours to dry at room temperature. Between measurements, the sensor was left in the air at room temperature. The lifetime of the sensor depended on the complexity of the matrix but up to 60 measurements were performed with the same sensor.

Procedure

Screen-printed microsensor with DDA-TPB as sensing material was used for all potentiometric measurements.

The four concentrations of CPC solutions: $4 \cdot 10^{-3}$ mol dm⁻³, $1 \cdot 10^{-3}$ mol dm⁻³, $1 \cdot 10^{-4}$ mol dm⁻³, $5 \cdot 10^{-5}$ mol dm⁻³, were used as titrants. As analytes during the potentiometric titrations, NaDDS and NaDBS were used. For all the titrations, the volume of the solution used was 25 cm³.

The concentration of AS was determined in five different samples of industrial effluents. The samples were diluted before the measurements, there was no ionic strength adjustment, and the pH was adjusted to 3 in all the measurements to avoid the simultaneous titration of soaps if present and ASs. In order to determine the accuracy and precision of the measurements, the standard addition method was used, where NaDDS was added at two concentration levels.

The titrator was programmed to DET Mode (Dynamic Equivalence point Titration) with equilibrium time of 30 s and signal drift of 5 mV min⁻¹. The wait time before the start of the titration was 120 s. All the measurements and titrations were conducted at room temperature using a magnetic stirrer and without ionic strength adjustment or pH adjustment (except for the industrial effluent titrations, in which the pH was adjusted to 3).

The MBAS method[4] was used as a standard method.

The influence of pH on the potentiometric titrations was examined over a pH range of 2 to 10 in solutions of NaDDS and NaDBS at a concentration of $4 \cdot 10^{-3}$ mol dm⁻³. The pH values of 2, 3, 5, 8 and 10 were adjusted with buffers.

The influence of the ionic strength on the potentiometric titration was examined by adding NaDDS ($c = 4 \cdot 10^{-3}$ mol dm⁻³) as the analyte in a sodium sulfate solution at the following three concentrations: 0.001 mol dm⁻³, 0.01 mol dm⁻³ and 0.1 mol dm⁻³ (the ionic strengths were between 0.003 and 0.300) and CPC ($c = 4 \cdot 10^{-3}$ mol dm⁻³) was used as the titrant.

Results and discussion

Response characteristics

The Nernst equation describes the electromotive force of the sensor immersed in the solution of AS:

$$E = E^0 + S \cdot \log a_{AS-} \tag{1}$$

where: E^0 – constant potential term, S – sensor slope, a_{AS-} – activity of surfactant anion.

The activity coefficients were calculated using the Davies equation. Dynamic response of SPMS microsensor toward NaDDS and NaDBS in concentration range $1 \cdot 10^{-7}$ mol dm⁻³ to $5 \cdot 10^{-4}$ mol dm⁻³ are shown in Figure 1. The sensor responded within 60 s for low concentration range of NaDBS, and within 20 s for low concentration of NaDDS. For higher
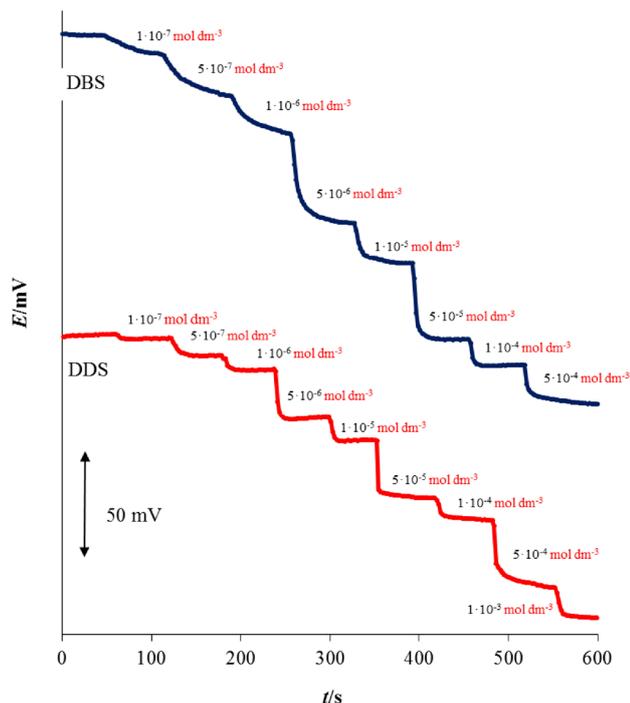
Fig. 1 – *Dynamic response characteristics of DDA-TPB based SPMS in NaDDS and NaDBS solutions. Here and in the following figures, the curves are displaced laterally or vertically for clarity.*

Fig. 2 – *Influence of pH on the curve of potentiometric titration of NaDDS solution ($c = 4 \cdot 10^{-3}$ mol dm^{-3}), and their first derivative using SPMS microsensor as the end point indicator and CPC ($c = 4 \cdot 10^{-3}$ mol dm^{-3}) as the titrant (● no pH adjustment, ● pH = 10, ● pH = 8, ● pH = 5, ● pH = 3, ● pH = 2, — no pH adjustment, — pH = 10, — pH = 8, — pH = 5, — pH = 3, — pH = 2)*

concentrations of NaDDS and NaDBS, SPMS microsensor responded within 5 s.

Interferences

The influence of pH

The influence of pH on the shape of the titration curve of both AS (NaDDS and NaDBS) using a SPMS microsensor as indicator of the end point titration was investigated. The resulting titration curves and their first derivatives for NaDDS and NaDBS are shown in Figures 2 and 3. It is evident that the electrode potential jumps at the points of inflection at all tested pH values are sufficiently large and sharp, allowing reliable detection of the end point. Slightly higher jumps in electrode potential inflection points were recorded in the neutral and alkaline range.

The influence of ionic strength

In order to investigate the influence of ionic strength, the series of Na$_2$SO$_4$ solutions of different ionic strengths were prepared. For the $4 \cdot 10^{-3}$ mol dm^{-3} solution of NaDDS, the adjusted ionic strengths were 0.301, 0031 and 0.003.

There was no significant difference between the measurements performed in water and in series of Na$_2$SO$_4$ solutions with different ionic strength (Figure 4). The results confirmed that the DDA-TPB *screen-printed* microsensor is suitable for measurements in commercial products with different ionic strength.
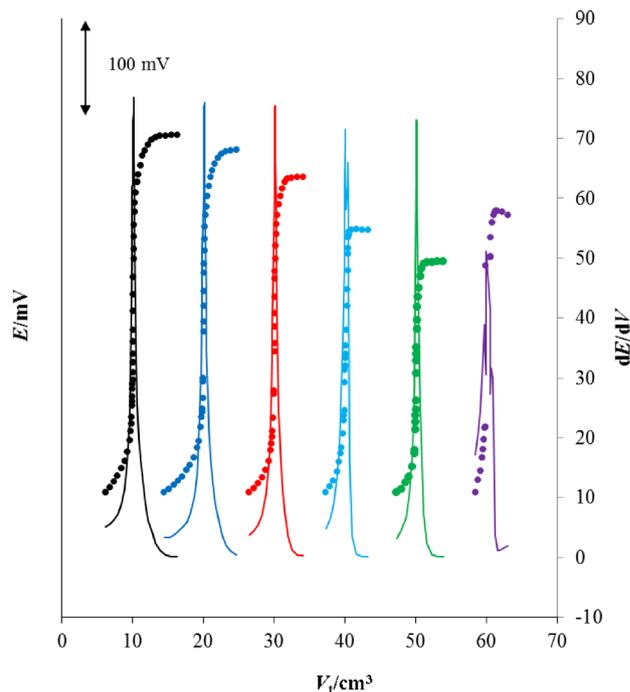

Fig. 3 – *Influence of pH on the curve of potentiometric titration of NaDBS solution ($c = 4 \cdot 10^{-3}$ mol dm^{-3}), and their first derivative using SPMS microsensor as the end point indicator and CPC ($c = 4 \cdot 10^{-3}$ mol dm^{-3}) as the titrant (● no pH adjustment, ● pH = 10, ● pH = 8, ● pH = 5, ● pH = 3, ● pH = 2, — no pH adjustment, — pH = 10, — pH = 8, — pH = 5, — pH = 3, — pH = 2)*
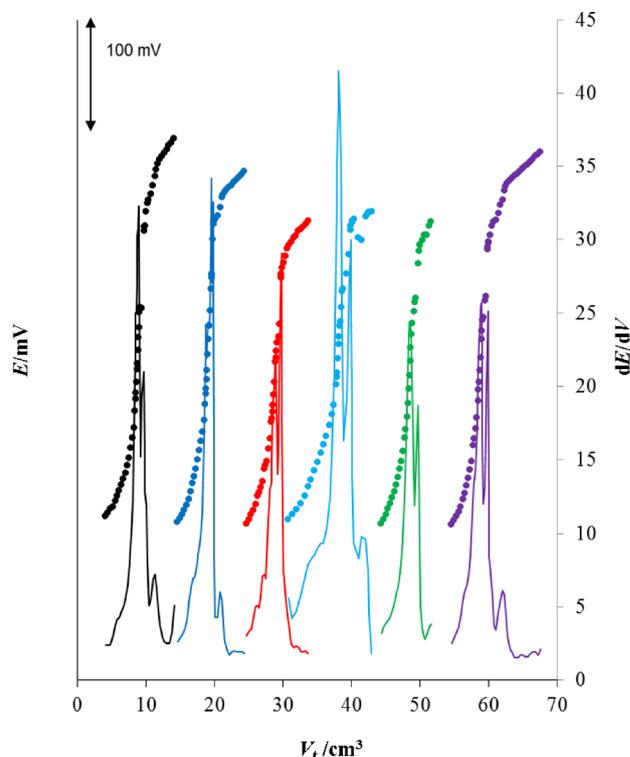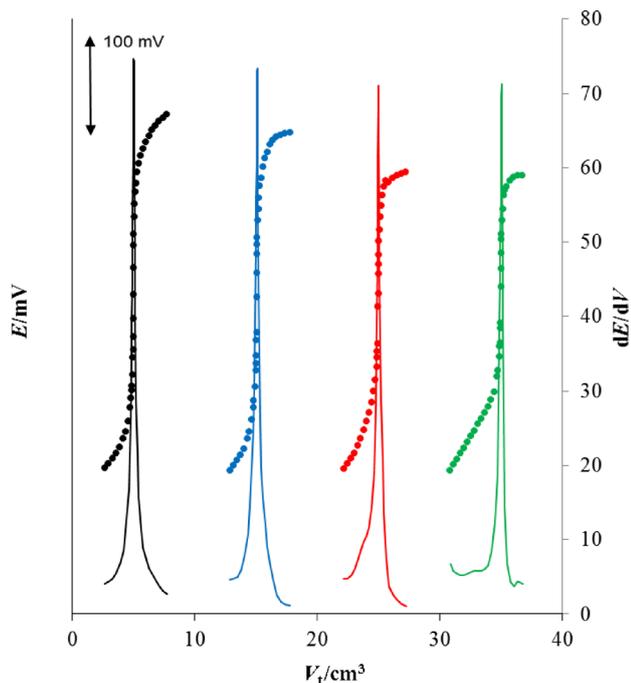
Fig. 4 – *Influence of ionic strength on potentiometric titration curve of NaDDS (c = 4·10⁻³ mol dm⁻³), and their corresponding first derivatives using SPMS sensor as indicator and CPC (c = 4·10⁻³ mol dm⁻³) as the titrant (● no ionic strength adjustment, ● Na₂SO₄ (c = 1·10⁻³ mol dm⁻³), ● Na₂SO₄ (c = 1·10⁻² mol dm⁻³) ● Na₂SO₄ (c = 1·10⁻¹ mol dm⁻³), — no ionic strength adjustment, — Na₂SO₄ (c = 1·10⁻³ mol dm⁻³) , — Na₂SO₄ (c = 1·10⁻² mol dm⁻³), — Na₂SO₄ (c = 1·10⁻¹ mol dm⁻³)*
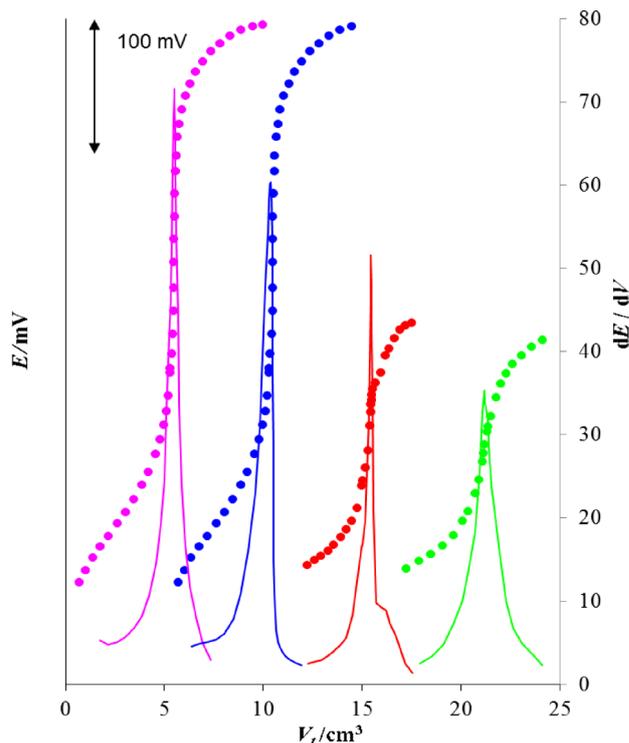

Fig. 5 – *Potentiometric titration curves of NaDDS and their corresponding first derivatives using SPMS microsensor as detector and CPC as titrant of the following concentrations: ● 4·10⁻³ mol dm⁻³, ● 1·10⁻³ mol dm⁻³, ● 1·10⁻⁴ mol dm⁻³, ● 5·10⁻⁵ mol dm⁻³, — 4·10⁻³ mol dm⁻³, — 1·10⁻³ mol dm⁻³, — 1·10⁻⁴ mol dm⁻³, — 5·10⁻⁵ mol dm⁻³*

Potentiometric titration

Selection of titrant concentration

The previous investigations showed that CPC is the best titrant for both AS (NaDDS and NaDBS)[22].

In order to find the lowest concentration of the titrant that will give still a sufficiently expressed, analytically usable point of inflection, a series of different titrant concentrations were investigated. The low concentration of titrant would enable the determination of very low concentrations of AS, that are usually present in industrial wastewater. For this purpose, a series of titrant solutions at four concentration levels $4·10^{-3}$ mol dm⁻³, $1·10^{-3}$ mol dm⁻³, $1·10^{-4}$ mol dm⁻³ and $5·10^{-5}$ mol dm⁻³ were tested. The solutions of NaDDS and NaDBS covering the concentration range between 10^{-4} and 10^{-6} mol dm⁻³ were used. The resulting titration curves for NaDDS and NaDBS are shown in Figures 5 and 6. All titration curves, including those obtained using $5·10^{-5}$ mol dm⁻³ CPC titrant, show a satisfactory potential jump that provides a reliable location of the end point. The magnitude of potential jumps at titration of NaDDS ranged from 290 mV for $4·10^{-3}$ mol dm⁻³ CPC to 100 mV for $5·10^{-5}$ mol dm⁻³ CPC, whereas those for NaDBS ranged between 240 mV and 100 mV for the same titrant concentrations.
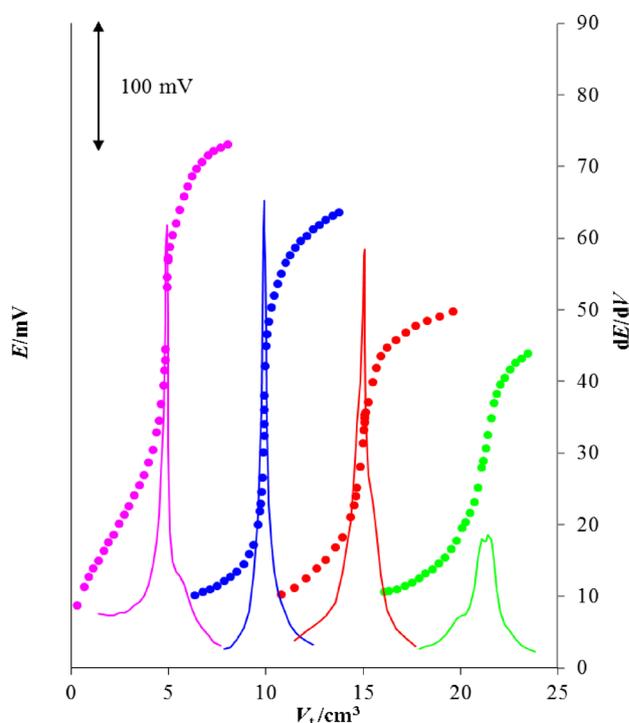

Fig. 6 – *Potentiometric titration curves of NaDBS and their corresponding first derivatives using SPMS microsensor as detector and CPC as titrant of the following concentrations: ● 4·10⁻³ mol dm⁻³, ● 1·10⁻³ mol dm⁻³, ● 1·10⁻⁴ mol dm⁻³, ● 5·10⁻⁵ mol dm⁻³, — 4·10⁻³ mol dm⁻³, — 1·10⁻³ mol dm⁻³, — 1·10⁻⁴ mol dm⁻³, — 5·10⁻⁵ mol dm⁻³*

The consumption of titrant at the end point was calculated from the derivative curve.

Titration of technical grade anionic surfactants

The two most commonly used technical grade ASs (NaDDS and NaDBS) were potentiometrically titrated using CPC as titrant.

The new DDA-TPB based polymeric membrane sensor (PMS) and SPMS were used as titration end-point detectors. The curves of potentiometric titration of two technical ASs using both sensors are shown in Figure 7. There were practically no differences in the shape and magnitude of inflexion of the resulting titration curves, regardless of which surfactant sensor was used.

Titration of wastewater

For this investigation, five industrial wastewater samples were taken. Samples were collected in different places and at different times. Before measurement, the samples were diluted and optionally filtered, without adjusting the ionic strength, the pH value was set to 3. In order to determine the accuracy and precision of potentiometric titration determination, the standard addition method was used, the results are shown in Table 1. Curves of potentiometric titration of five in-

Table 1 – *Results of the potentiometric titrations of the industrial wastewater with the addition of known concentrations of NaDDS using the SPMS DDA-TPB based surfactant sensor as the indicator and CPC as the titrant*

Wastewater sample	Calculated AS (mol dm^{-3})*	NaDDS		
		Added (mol)	Found* (mol)	Recovery (%)
1	$5.19 \cdot 10^{-4}$	$8 \cdot 10^{-6}$	$8.2 \cdot 10^{-6}$	102.6
		$2 \cdot 10^{-5}$	$1.99 \cdot 10^{-5}$	99.4
2	$9.32 \cdot 10^{-6}$	$2 \cdot 10^{-7}$	$2.07 \cdot 10^{-7}$	103.4
		$5 \cdot 10^{-7}$	$4.93 \cdot 10^{-7}$	98.6
3	$5.90 \cdot 10^{-4}$	$8 \cdot 10^{-6}$	$8.52 \cdot 10^{-6}$	106.5
		$2 \cdot 10^{-5}$	$2.03 \cdot 10^{-5}$	101.6
4	$8.86 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	$2.04 \cdot 10^{-7}$	101.9
		$5 \cdot 10^{-7}$	$5.03 \cdot 10^{-7}$	100.5
5	$5.42 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	$1.96 \cdot 10^{-7}$	98.1
		$5 \cdot 10^{-7}$	$5.07 \cdot 10^{-7}$	101.4

*average of 5 determinations

dustrial wastewater samples with known addition of NaDDS, using PMS sensor and SPMS microsensor as detector of end-point, are shown in Figure 8.
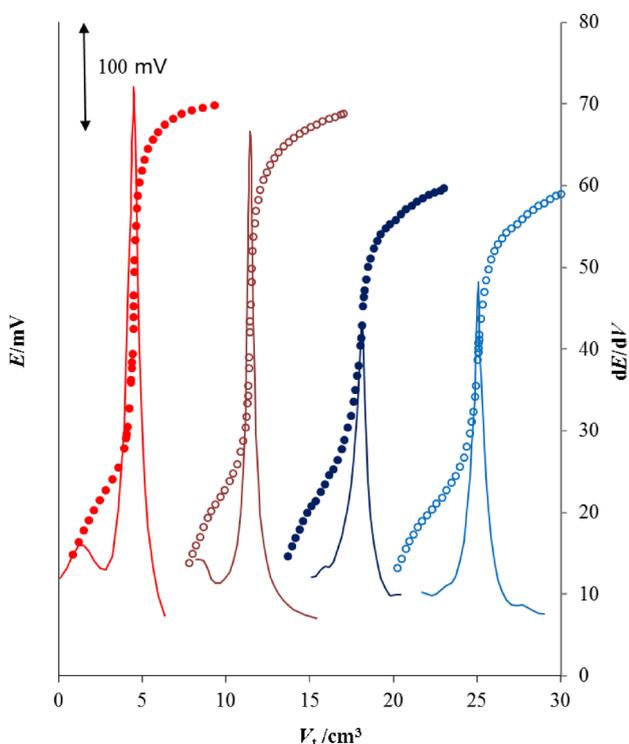

Fig. 7 – *Potentiometric titration curves of technical grade AS (NaDDS and NaDBS) and their corresponding first derivatives, using PMS and SPMS sensors as the indicator and CPC (c = 4·10^{-3} mol dm^{-3}) as titrant (● NaDDS-PMS, ○ NaDDS-SPMS, ● NaDBS-PMS, ○ NaDBS-SPMS, — NaDDS-PMS, — NaDDS-SPMS, — NaDBS-PMS, — NaDBS-SPMS)*
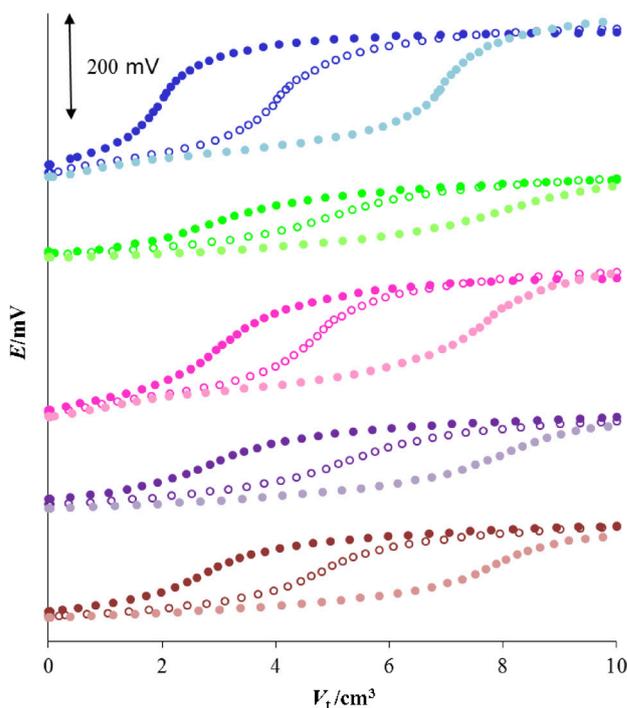

Fig. 8 – *Potentiometric titration curves of five industrial wastewater samples with known addition of NaDDS using SPMS microsensor as endpoint detector (● sample 1, ○ sample 1 + 2 cm³ NaDDS, ● sample 1 + 5 cm³ NaDDS, ● sample 2, ○ sample 2 + 2 cm³ NaDDS, ● sample 2 + 5 cm³ NaDDS, ● sample 3, ○ sample 3 + 2 cm³ NaDDS, ● sample 3 + 5 cm³ NaDDS, ● sample 4, ○ sample 4 + 2 cm³ NaDDS, ● sample 4 + 5 cm³ NaDDS, ● sample 5, ○ sample 5 + 2 cm³ NaDDS, ● sample 5 + 5 cm³ NaDDS)*

Table 2 – *Results of potentiometric titrations of the industrial wastewater obtained using CPC (c = 0.1 mmol dm⁻³) as titrant and PMS and SPMS as end-point detectors compared with those obtained using MBAS method*

Wastewater sample	Concentration of AS (mg dm⁻³)*		
	SPMS	PMS**	MBAS
1	145.54 ± 4.38	147.44 ± 2.70	139.2
2	2.65 ± 0.04	2.64 ± 0.02	2.42
3	175.65 ± 6.43	176.67 ± 3.28	168.2
4	25.40 ± 0.07	24.43 ± 0.83	23.72
5	14.21 ± 0.26	15.24 ± 0.31	14.19

* mean ± confidence interval ($p = 95$ %), number of measurements n = 5

**reference 19

For the sake of comparison, the AS concentration was determined using standard MBAS method also. Table 2 shows the results of potentiometric titration of industrial wastewater obtained using CPC ($c = 0.1$ mmol dm⁻³) as titrant, and PMS and SPMS sensors as detectors, compared with the results obtained by standard MBAS method.

The results are expressed as NaDBS concentration, conventionally used as a standard at MBAS method. It can be concluded that there is satisfactory agreement of the results obtained using SPMS sensor and standard MBAS method.

Conclusion

A new, sensitive, accurate, fast, simple, and inexpensive AS responsive *screen-printed* potentiometric microsensor based on DDA-TPB ion-exchange complex as the sensing element in a PVC-membrane was used as the end-point detector during the potentiometric titrations of low levels of AS. The solutions containing low levels of AS were successfully titrated with CPC as titrant.

The pure NaDDS and NaDBS solutions and five samples of industrial wastewater were successfully titrated. Titration curves for NaDDS and NaDBS revealed strong inflection even at a low titrant concentration of $5 \cdot 10^{-5}$ mol dm⁻³.

The obtained potentiometric titration curves exhibited clearly defined inflections enabling reliable equivalence point detection using the first derivative method.

The results obtained by MBAS were compared with those obtained by the DDA-TPB based sensor and showed a satisfactory correlation.

The ASs in effluents were successfully titrated across a pH range of 2 to 10. The ionic strength of the analyte did not influence the potentiometric titrations.

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