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Journal of Chromatography A, 781 (1997) 541–545

JOURNAL OF CHROMATOGRAPHY A

Short communication

Capillary electrophoresis as a routine industrial tool for quantitative analytical testing
Determination of sodium dimethyldithiocarbamate in effluents

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Abstract

The determination of a specific anionic species (sodium dimethyldithiocarbamate) in waste water was performed by capillary electrophoresis with direct UV detection. The application of new technology sulfonic acid polymer-coated capillary columns achieved sensitive analysis with robust electroosmotic flow (EOF), where other coated columns and conventional fused-silica had failed due to analyte adsorption problems. Optimum conditions for the separation of cationic, neutral, and other anionic species, including quantitative analyses of the analyte of interest, were obtained. The relative standard deviations for the analysis of anions were found to be 2.7 and 12.8% for 528 and 37 μg/ml concentrations, respectively. The detection limit for sodium dimethyldithiocarbamate in waste water was established at 1 μg/ml for typical sample size (2 ml) without preconcentration of the analyte. The usefulness of capillary electrophoresis as a routine industrial monitoring tool was successfully demonstrated. © 1997 Elsevier Science B.V.

Keywords: Industrial chemicals; Sodium dimethyldithiocarbamate; Carbamates; Anions

1. Introduction

The use of industrial ionic chemicals such as the sodium salt of dimethyldithiocarbamate (SDMDTC) is quite prolific for many specific chemical processes [1]. These water-soluble materials are frequently eliminated with process effluents. This necessitates sensitive and accurate determinations of the ionic species for effective pollution-abatement procedures. The concentration of these species can be monitored by conventional spectrophotometric tests, but these tests are non-differentiating and subject to gross interferences from many sources. Alternatively, the determination of the SDMDTC ionic species by HPLC methods has not been effective at efficiently resolving the various ionic compounds found to be present. This work describes the separation of anionic species by the use of capillary electrophoresis employing sulfonic acid polymer-coated column technology, robust electroosmotic flow (EOF), and normal polarity techniques (cathode at the detector end). This approach is different from conventional coated column capillary electrophoresis with reverse polarity which eliminates EOF to overcome the inherent reverse migration of the analytes of interest [2]. The reverse polarity approach works well for the SDMDTC material qualitatively, however, adsorption of the analyte onto the coated column wall prevents accurate quantification. This technique would otherwise be desirable because

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0021-9673/97/$17.00
PII S0021-9673(97)00634-1

unwanted neutral species and cations are screened from the analysis due to the inherent properties of coated column technology and applied reverse-polarity electrical field [3,4]. The solutions to overcoming inherent obstacles encountered in the CE analysis of anions has been thoroughly discussed by many sources [5–7].

The analysis of inorganic anions and small organic anions by capillary electrophoresis has been well established as routine by Stahl [8], and as versatile for the analysis of many anionic components by Jones and Jandik [9]. SDMDTC, a hydrophilic non-aromatic anion, exhibits UV adsorption at 254 nm, and is well suited for capillary electrophoretic analysis. The chemical structure of SDMDTC is as follows: $(CH_3)_2$–N–C(S)–$S^{-}{}^{+}$Na.

Tindall and Perry demonstrated the separation of fast anions without flow reversal for small inorganic anions using commercial coated column technology [10], and the authors have successfully applied this column technology to the analysis of naphthalene sulfonates in waste water [11]. This approach is not applicable to the analysis of SDMDTC because the fused-silica column is subject to analyte adsorption problems with hydrophilic substances like SDMDTC, primarily due to hydrogen bonding. This adsorption has been measured at 3 pg of injected sample. The adverse affects of the column wall–analyte interaction are significantly reduced upon the use of a sulfonic acid-coated capillary. The sulfonic acid capillary exhibits EOF proportional to the amount of coating and is largely independent of pH. The synthesis and evaluation of these anionic polymer-coated capillaries is described by Peng et al. [12].

The primary aim of this work is to apply CE as a routine, robust and viable tool for analytical testing in the chemical industry, used in the same way that HPLC is applied with appropriate statistical reliability.

2. Experimental

2.1. Apparatus and conditions

The CE system used for this study was the Beckman P/ACE 5000 Capillary Electrophoresis instrument, equipped with a variable-wavelength UV detector (filtered) and System Gold software integration package (Beckman Instruments, Fullerton, CA, USA). A sulfonic acid high-EOF coated column of 37 cm×50 μm I.D. from Scientific Resources (SRI, Eatontown, NJ, USA), was employed to effect the separations. The detector window was located 30 cm from the injection end of the capillary column. The CE electrical configuration was in normal polarity mode (anode at the detector end) using a constant current mode set at 50 μA (approximately 26 kV required).

New capillary columns were conditioned by rinsing with run buffer for 30 min, followed by a 5-min HPLC-grade water rinse, and a second rinse (10 min) with the run buffer solution. A 1-min rinse of run buffer solution preceded each sample and standard run and was followed by a 6-min rinse of 0.1% *p*-toluene sulfonic acid (PTSA, Aldrich, Milwaukee, WI, USA), a 2-min rinse of water, and a 2-min rinse of run buffer. The analysis run buffer solution was 25 m*M* sodium phosphate, pH 6.5, from Scientific Resources. The pH is critical because a pH higher than 7.0 will degrade the sulfonic acid polymer coating. A pH lower than 3.5 will be lower than the p*K* of SDMDTC.

Pressure sampling was employed for 15 s using a pressure of 3.4 kPa to inject approximately 33 nl of sample or standard. This was followed by an injection of the sodium phosphate electrolyte for 1 s at 3.4 kPa for a 2 nl buffer slug to eliminate diffusion of the sample into the injection run buffer vial. The column was maintained at 25°C via the liquid cooling capability of the P/ACE system.

Detection for electropherograms was achieved at 254 nm and an absorbance range of 0.2 AUFS and was employed for all CE quantitative work.

2.2. Sample preparation

Samples were prepared by filtering a 2.0-ml sample aliquot with a 0.2-μm PTFE membrane (syringe type, Scientific Resources). The 2.0 ml of filtrate was diluted to 4.5 ml by adding 2.5 ml of internal standard solution.

2.3. Quantitation

Quantitation was achieved daily with a five-point

linear calibration curve of the SDMDTC at a concentration range of 838 to 0.8 μg/ml. The calibration curve was generated by the response of SDMDTC at 254 nm (SDMDTC λ-max). Analyte peak areas are automatically corrected for anion mobility velocity changes by referencing the internal standard mobility. The analysis time is 12 min.

2.4. Reagents

All standard solutions were prepared by diluting 838 μg/ml stock solution containing the analyte, sodium salt of dimethyldithiocarbamate (Uniroyal Chemical, Middleburg, CT, USA). Samples were prepared with de-ionized water filtered by a HPLC-grade water filtration system (Millipore, Bedford, MA, USA). The internal standard, 2-hydroxybenzoic acid (Aldrich, Milwaukee, WI, USA) was prepared as a 100 μg/ml solution and used for all samples and standards.

3. Results and discussion

3.1. Separation

Robust EOF at moderate pH (6.5) from a commercially available buffer, a medium length coated capillary, and an internal standard accounts for the simple determination of the SDMDTC by CE. Fig. 1 shows a standard electropherogram and Fig. 2 shows a sample electropherogram. The EOF was measured at 9.375 cm/min. The apparent mobility of SDMDTC is calculated as 7.41×10^{-5} $cm^2/V\,s$ and the apparent mobility of the *p*-hydroxybenzoic acid internal standard is calculated as 6.66×10^{-5} $cm^2/V\,s$.

A five-level calibration curve with duplicate injections of standard SDMDTC gave a linear calibration over the concentration range of interest for SDMDTC. The linear regression for the calibration curve is typically: $y=0.007x+0.0967$ ($y=mx+b$ format, where x is the concentration of SDMDTC in

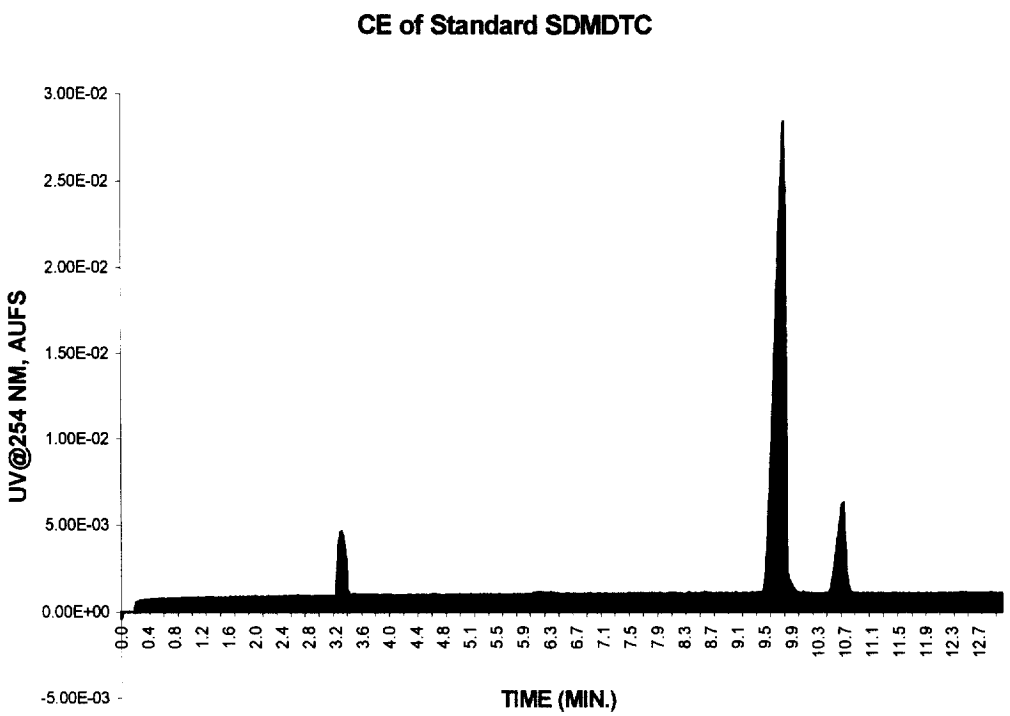

Fig. 1. Analysis of SDMDTC standard (10.7 min) separated from the *p*-hydroxybenzoic acid internal standard (9.6 min). Analytical conditions: capillary, sulfonic acid (high-EOF)-coated fused silica (37 cm×50 μm I.D.); electrolyte, 25 m*M* sodium phosphate buffer (pH 6.5); constant current mode, 50 μA (approximately 26 kV applied); detection, UV absorbance at 254 nm.

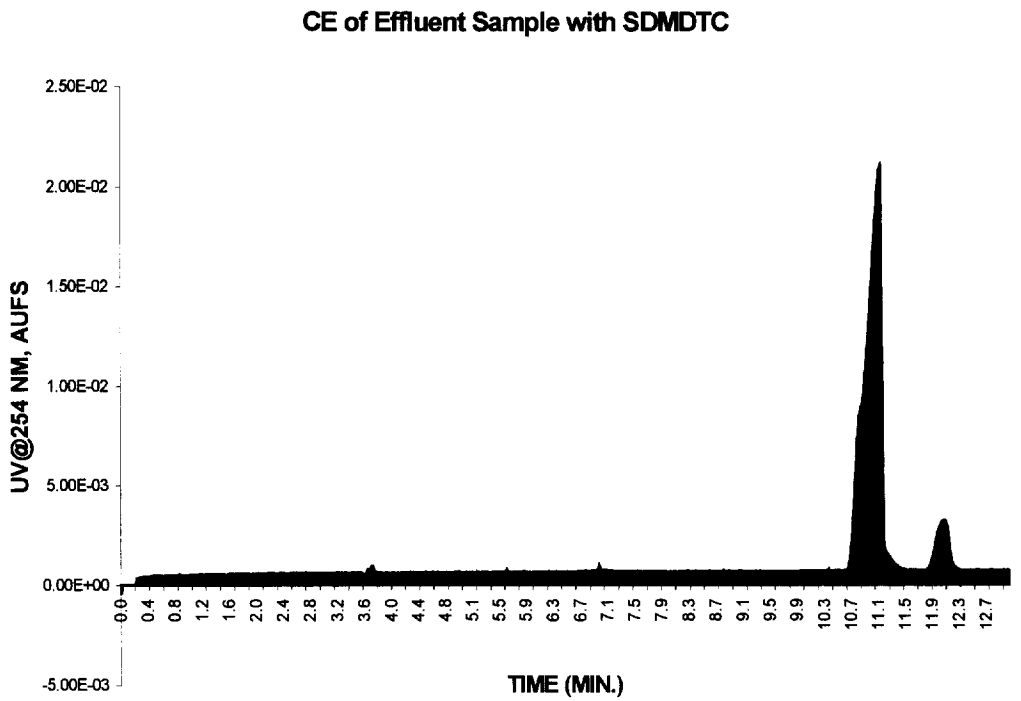

Fig. 2. Analysis of three sample composite effluent containing 528 μg/ml of SDMDTC (12.0 min) separated from the *p*-hydroxybenzoic acid internal standard (10.9 min) and other minor sample impurities. Analytical conditions: capillary, sulfonic acid (high-EOF)-coated fused silica (37 cm×50 μm I.D.); electrolyte, 25 m*M* sodium phosphate buffer (pH 6.5); constant current mode, 50 μA (approximately 26 kV applied); detection, UV absorbance at 254 nm.

mg/ml and y is the unitless corrected peak area from the Beckman System Gold software package). Standard concentrations ranged from 838 to 0.8 μg/ml, sufficient to cover more than 50–150% of the normal sample concentration range. Correlation coefficients greater than $0.999x$ are typical using a least-squares linear regression method. This method is sensitive to 1.0 μg/ml with stringent analysis controls and routinely to 10.0 μg/ml.

Some variation in the apparent mobilities of the analyte and the internal standard has been observed. Adverse effects of this variability are minimized by employing the internal standard to correct for analyte velocities (past the detector window). This phenomenon is most likely due to high salt concentrations in the sample relative to the CE electrolytic buffer concentration and could be minimized further by increasing the buffer system concentration. The phosphate buffer used in this work was purposely left at the concentration in which it was purchased, to facilitate the overall goal of the experiment: simplicity for routine testing. The effect of high concentrations of salt in samples on the CE analysis of anions has been thoroughly discussed by Song et al. [13].

3.2. Statistics

The calculations for repeatability (intra-day precision) and reproducibility (inter-day precision) were based on the assay values of three samples of SDMDTC-spiked composite waste effluent. The initial concentration of stock standard of 838 μg/ml was diluted with the composite waste effluent to make three samples; concentrations corresponded to the low (37 μg/ml), medium (113 μg/ml), and high (528 μg/ml) points of the calibration curve. This was accomplished using five replicates of each sample analyzed each day for 3 days. The CE test solutions were injected in duplicate and corrected peak areas were averaged. Table 1 displays these statistical calculations for repeatability and repro-

Table 1
SDMDTC assay variability for CE test (in %R.S.D.)

Effluent sample (μg/ml)	Day 1	Day 2	Day 3	Inter-day	Average
528	2.4	2.0	4.2	2.7	520
113	3.7	4.3	3.7	3.8	107
37	8.9	7.7	8.0	12.8	39

Table 2
SDMDTC assay accuracy for CE test (percent of target value)

Effluent sample (μg/ml)	Day 1	Day 2	Day 3	Average	Accuracy (%)
528	520	506	534	520	98.5
113	111	103	108	107	95.0
37	34	40	44	39	106.0

ducibility in %R.S.D. The intra-day precision values of SDMDTC were found to be 2.5% R.S.D. for 528 μg/ml concentrations ranging to 3.9% R.S.D. for 113 μg/ml concentrations and 8.2% for 37 μg/ml levels of SDMDTC. Table 1 displays these statistical calculations for repeatability in %R.S.D. in greater detail. Calculations for inter-day precision are comparable to the intra-day precision statistics except at the lowest concentrations of SDMDTC. Day-to-day precision for lower levels of SDMDTC is apparently not as good as daily precision values. Table 2 displays these statistical calculations and values for accuracy in percent of targeted sample values of SDMDTC in greater detail.

4. Conclusions

CE using conventional free solution CE techniques and commercially available sulfonic acid-coated fused-silica columns provides rapid, efficient, and accurate analysis of the polymerization short-stop, the sodium salt of dimethyldithiocarbamate in waste water. Arduous sample preparations are not necessary, cations and neutral species do not interfere, and anionic chemicals are separated from the analyte. This method provides level of confidence in the determination of SDMDTC in industrial effluents and demonstrates the practical utility of CE as a routine analytical tool. The accuracy of this procedure is calculated to be better than 95% within targeted values in the working range of the calibration curve.

Acknowledgments

The authors wish to thank Robert Weinberger of CE Technologies for helpful discussions concerning analyte–column wall absorption problems.

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