



ELSEVIER

Journal of Chromatography A, 671 (1994) 445-451

JOURNAL OF  
CHROMATOGRAPHY A

## Determination of inorganic sulfate in detergent products by capillary electrophoresis

James M. Jordan\*, R. Laura Moese, R. Johnson-Watts, D. Edward Burton

*The Procter and Gamble Company, 6060 Center Hill Avenue, Cincinnati, OH 45224, USA*

### Abstract

We have been able to show that capillary electrophoresis (CE) can be used for the rapid determination of sulfate in granular detergents. With this method, an aqueous solution of the detergent (5 g/l) is prepared and a small, filtered (0.2  $\mu\text{m}$ ) portion is used for the assay. The total analysis time per sample by CE is less than 15 min using duplicate injections, with 2-min washes between each injection. The analytical method and a comparison of results between CE and gravimetric determinations, will be discussed. Sodium sulfate was quantitated by CE and by a  $\text{BaCl}_2$  gravimetric method using 26 different granular detergents with levels ranging from 2 to 40%  $\text{Na}_2\text{SO}_4$ . A least squares fit of the gravimetric data plotted *versus* the CE data resulted in  $r^2 = 0.991$ ,  $m = 0.92 \pm 0.02$  and  $b = -0.41 \pm 0.24$  (SEE = 0.864), where  $m$  = slope,  $b$  =  $y$ -intercept, and SEE = standard error of estimate. Day-to-day CE results varied by less than 1.0%  $\text{Na}_2\text{SO}_4$ . Within a given day, results from replicate samples varied typically by less than 0.5%  $\text{Na}_2\text{SO}_4$ . The optimum linear range for this method is between 10 to 100  $\mu\text{g/ml}$ , even though the response is linear up to and beyond 180  $\mu\text{g/ml}$ . Sulfate concentrations above 100  $\mu\text{g/ml}$  result in poor resolution for samples with multiple ions.

### 1. Introduction

This paper describes the use of a technique for the determination of low-molecular-mass ionic analytes by capillary electrophoresis (CE), using indirect ultraviolet detection. In particular, we have selected an approach developed for the determination of small inorganic anions using an electrolyte composed of chromate and a quaternary amine electroosmotic flow modifier to affect separation, as first reported by Jones and Jandik in 1990 [1,2]. This approach has proven successful especially for the determination of anions in complex samples such as Kraft black liquors in the pulp and paper industry [3], bulk pharmaceuticals and their synthetic intermediates [4] and prenatal vitamin formulations [5].

Since laundry detergents also represent complex mixtures of organic and inorganic components, this same approach was selected for determining sulfate. Laundry detergents typically include surfactants (anionic, cationic, non-ionic and/or amphoteric), organic chelating agents (*i.e.* EDTA), oxidizing agents (*i.e.* sodium perborate), optical brighteners, enzymes, water/solvents and inorganic salts such as sodium carbonate, sulfate, chloride, silicate and borax. The quantitation of sodium sulfate in detergent products can be a long and tedious process using well known gravimetric determinations. The usual approach for quantitating sulfate in detergent products is by a gravimetric method using barium chloride [6,7], which can require 3 to 4 days per sample to complete, depending on how easily the samples can be vacuum filtered.

Although ion chromatography may be consid-

\* Corresponding author.

ered as an alternative to gravimetric methods, the cost involved in personnel training and instrument maintenance is a serious consideration, and still some preparation is needed for detergent samples. We were interested in determining if CE would provide us a fast and simple means for the rapid quantitation of sulfate, thereby providing a significant improvement in our lab's productivity.

## 2. Experimental

### 2.1. Instrumentation

A Quanta 4000 CE system (Waters Chromatography Division of Millipore, Milford, MA, USA) equipped with a 60 cm  $\times$  75  $\mu$ m I.D. fused-silica capillary (Waters AccuSep CE capillary assembly), a Hg lamp with 254-nm filters and negative power supply was employed for all experiments. Data acquisition and processing was performed using a Waters 860 Chromatography Data System on a MicroVax 3100 Computer (Digital Equipment Corp., Maynard, MA, USA). A Waters Laboratory Acquisition and Communications/Environment (LAC/E) module was used to connect the data system and CE instrument over Ethernet and is interfaced with the host computer for data archiving and processing. The LAC/E module receives the analog signal from the CE instrument through a Waters SAT/IN (Satellite Interface) module, which is an A/D converter. The CE instrument detector output is connected directly to the SAT/IN module with inverted signal polarity. The CE detector time constant was set at 0.1 s with a data acquisition rate of 20 Hz. Data collection was initiated by a signal cable connection between the Quanta 4000 and the SAT/IN module.

### 2.2. Reagents

Sodium chromate tetrahydrate (analytical-reagent grade), Ultrex and reagent-grade sulfuric acid were obtained from J.T. Baker (Phillipsburg, NJ, USA). Sodium sulfate, 99.99 + %

pure, sodium hydroxide, potassium hydroxide and barium chloride were obtained from Aldrich (Milwaukee, WI, USA). A bromide standard solution (500  $\mu$ g/ml) was obtained from HACH Co. (Loveland, CO, USA). Waters CIA-Pak OFM Anion-BT solution was obtained as a 20 mM concentrate from the Waters Division of Millipore. Purified water (18 M $\Omega$ ) was obtained using a Millipore Milli-Q Plus water purification system (Bedford, MA, USA) and this water was used for preparing all solutions.

### 2.3. Solutions

Electrolyte solutions were prepared daily, filtered using a 0.45- $\mu$ m Millipore membrane (type HV) disposable syringe filter, and degassed with a Waters solvent clarification kit. Solutions of 100 mM KOH were used for pre-conditioning the capillary daily. A chromate electrolyte concentrate was prepared by adding to a 1-l volumetric flask, 500 ml Milli-Q water, 23.41 g sodium chromate tetrahydrate and 68 ml of 10 mM sulfuric acid (prepared by diluting 560  $\mu$ l of concentrated sulfuric acid to 1 l using Milli-Q water). This concentrate may be stored in volumetric or sealed glass container for up to 1 year and will make 20 l of electrolyte. The working electrolyte solution was prepared by diluting 5 ml of the Waters OFM Anion-BT solution [8] and 7 ml of the electrolyte chromate concentrate to 100 ml. This results in a 5 mM chromate and 0.5 mM OFM electrolyte. The pH of the electrolyte may be adjusted as necessary to pH 8.0 with 100 mM NaOH.

Sulfate quantitation was based on external standard calibration. The sulfate standard solutions of 10, 30, 70 and 100  $\mu$ g/ml were prepared from dilutions of a 4000  $\mu$ g/ml concentrated standard. Duplicate injections at each level were used to calibrate the system.

The presence of bromide in the electrolyte, which is introduced by the OFM, causes a "dip" in the baseline at the migration time corresponding to bromide [9]. This could potentially interfere with the quantitation of chloride and sulfate so we have used a bromide diluent to eliminate this problem. The bromide standard

solution is used to prepare the diluent for the final dilution step of the samples. The diluent was prepared by diluting 30 ml of the 500  $\mu\text{g}/\text{ml}$  standard solution to 1 l. This results in approximately a 15  $\mu\text{g}/\text{ml}$  bromide spike in the samples.

The granular detergent samples should be riffled and ground before usage to ensure representative samples are taken. Sample solutions were prepared by dissolving 5 g of a detergent sample in 1 l of Milli-Q water. If the sample was known to have less than 5% sodium sulfate, 300  $\mu\text{l}$  of the 500  $\mu\text{g}/\text{ml}$  bromide stock was diluted to 10 ml using the sample solution (5 g/l) as diluent. For samples having more than 5% sodium sulfate, 1.0 ml of the sample solution was diluted to 10 ml using the 15  $\mu\text{g}/\text{ml}$  bromide diluent. A small portion of the spiked sample solution was then filtered using a disposable 5 ml syringe and a 0.2- $\mu\text{m}$  Gelman Ion Chromatography Acrodiscs (Ann Arbor, MI, USA) filter before being placed in the sample tray.

#### 2.4. Gravimetric procedure

The gravimetric procedure [7] for determining inorganic sulfate in laundry detergents is basically comprised of four steps: (1) alcohol separation, (2) removal of soluble silicates, (3) precipitation of sulfate with barium chloride and (4) weigh dry precipitate. For the alcohol separation, a 5-g sample of detergent was dissolved in hot ethanol and digested on a steam bath. Then the inorganic fraction was collected by vacuum filtration. This fraction was washed with concentrated hydrochloric acid, followed by evaporation to dryness and was repeated for a total of three iterations. The silicate was then separated by vacuum filtration. The filtrate was then diluted, and an aliquot taken and heated to boiling. At this point barium chloride was added to precipitate the sulfate. The precipitate was then separated by vacuum filtration and dried in a furnace.

#### 2.5. Electrophoretic conditions

Waters capillary ion electrophoresis (Waters' trade name: Capillary Ion Analysis) Method N-601 for general anions was used without modi-

fication [10]. The conditions used were 20 kV run voltage, hydrostatic injection at 10 cm height for 30 s, 254 nm detection, 0.1 s time constant, negative detector polarity, ambient temperature, 60 cm  $\times$  75  $\mu\text{m}$  I.D. fused-silica capillary and 5 min run time.

### 3. Results and discussion

Initial work with the CE method involved determination of the linear dynamic range for the quantitation of sulfate using standard solutions. Sulfate concentrations of 4, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140 and 180  $\mu\text{g}/\text{ml}$  were run with triplicate injections at each level. A least squares fit of the data through a zero intercept was linear over the entire range with  $r^2 = 0.9985$  and  $m = 300$ . A linear least squares fit with a non-zero intercept returned values of  $r^2 = 0.9994$ ,  $m = 292 \pm 2.0$  and  $b = 789 \pm 177$  (SEE = 379), where  $m$  = slope,  $b$  = y-intercept, and SEE = standard error of estimate. The working range was selected to be between 10–100  $\mu\text{g}/\text{ml}$  since resolution of the sulfate and chloride peaks begins to seriously deteriorate at levels approaching 100  $\mu\text{g}/\text{ml}$ . Typical calibration curves over this range have a correlation coefficient of  $r^2 = 0.9994$ .

To compare results from CE and gravimetric sulfate determinations, 26 laundry detergent samples with sulfate levels ranging from 2 to 40% were used for both methods. A typical electropherogram for a detergent sample is shown in Fig. 1. In this figure, the bromide spike

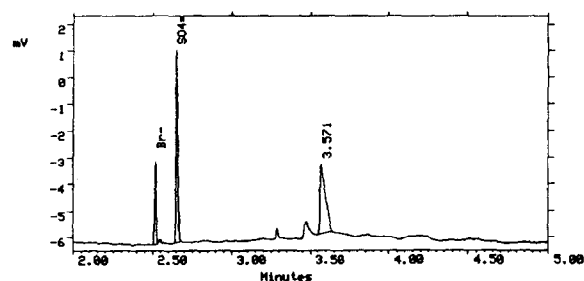


Fig. 1. Typical electropherogram for a detergent sample. In this figure, the bromide spike is readily identified and well separated from the sulfate peak, which represents approximately 20  $\mu\text{g}/\text{ml}$  sulfate.

is readily identified and well separated from the sulfate peak, which represents approximately 20  $\mu\text{g}/\text{ml}$  sulfate. The CE results for laundry detergent samples are summarized in Table 1. Compact and regular detergents refer to different types of detergent formulations. Typically, absolute day-to-day results varied by less than 0.5%  $\text{Na}_2\text{SO}_4$  by CE, and by not more than 2.0%. Replicate hydrostatic injections of the same sample typically varied by less than 0.05%. The day-to-day variability for some of these samples can be directly tied to particular detergent formulations for which it was difficult to obtain representative samples. To determine within-day variability, seven detergent samples were run in duplicate and the results are summarized in Table 2. As shown by the data, duplicate samples varied typically by less than 0.5%  $\text{Na}_2\text{SO}_4$  within a given day.

Gravimetric results are given in Table 3. Since the gravimetric determination is so labor intensive, typically only one sample is ever run for a sulfate determination. Duplicate gravimetric determinations are rarely performed on a daily basis unless some problem with a detergent formulation mass balance is identified. As seen by these results, gravimetric determinations can vary substantially, and this approach is very dependent on the skill of the analyst. Overall, the gravimetric method is very reliable, and results typically vary by less than 1%  $\text{Na}_2\text{SO}_4$ . A correlation plot of the %  $\text{Na}_2\text{SO}_4$  determined by the CE and gravimetric methods is shown in Fig. 2. A least squares fit of the data results in  $r^2 = 0.991$ ,  $m = 0.92 \pm 0.02$  and  $b = -0.41 \pm 0.24$  (SEE = 0.864). Examples of differences for several of the samples are given in Table 4 for comparison. As shown by the correlation plot,

Table 1  
Summary of CE results for day-to-day determinations of % sodium sulfate in 26 granular detergent products

Description	Day-to-day results, % $\text{Na}_2\text{SO}_4$	Average result, % $\text{Na}_2\text{SO}_4$	S.D.
Compact granule	2.0, 1.6, 1.7, 1.7	1.7	0.2
Compact granule	1.9, 2.1, 2.1	2.0	0.1
Compact granule	2.2, 2.2, 2.3	2.2	0.1
Compact granule	2.2, 2.2, 2.3	2.3	0.1
Compact granule	2.2, 2.4, 2.3	2.3	0.1
Compact granule	2.1, 2.9, 2.9, 2.5	2.6	0.5
Compact granule	2.6, 3.1, 3.1	2.9	0.3
Compact granule	2.9, 3.3	3.1	0.3
Compact granule	3.2, 3.6, 3.8	3.5	0.3
Compact granule	3.7, 3.8	3.8	0.1
Compact granule	4.0, 5.1, 4.0	4.4	0.6
Compact granule	4.8, 5.0	4.9	0.2
Compact granule	5.6, 4.3	5.3	0.2
Compact granule	5.7, 5.9	5.8	0.1
Compact granule	6.3, 6.3, 6.3	6.3	0.0
Compact granule	6.5, 6.5	6.5	0.0
Compact granule	6.7, 6.9	6.8	0.1
Compact granule	7.5, 7.1	7.3	0.3
Compact granule	8.7, 9.1	8.9	0.3
Compact granule	12.1, 13.1	12.6	0.7
Regular granule	13.5, 12.0, 12.7	12.7	0.8
Regular granule	16.4, 16.4, 16.7, 16.6, 16.2	16.5	0.1
Regular granule	18.7, 19.0	18.9	0.2
Regular granule	20.3, 19.7	20.0	0.4
Regular granule	22.8, 24.7	23.7	1.4
Regular granule	37.3, 36.7	37.0	0.4

Table 2

Summary of duplicate CE results for within-day determinations of % sodium sulfate in seven granular detergent products

Description	Within-day results, % Na <sub>2</sub> SO <sub>4</sub>	Average, % Na <sub>2</sub> SO <sub>4</sub>	S.D.
Regular granule	16.43, 16.66	16.55	0.16
Compact granule	5.59, 4.55	5.07	0.74
Compact granule	5.43, 4.82	5.13	0.43
Compact granule	2.07, 2.25	2.16	0.13
Compact granule	2.91, 2.86	2.89	0.04
Compact granule	2.51, 2.60	2.56	0.06
Compact granule	7.21, 7.50	7.36	0.20

Table 3

Summary of gravimetric results for day-to-day determinations of % sodium sulfate in 26 granular detergent products

Description	Day-to-day gravimetric results, % Na <sub>2</sub> SO <sub>4</sub>	Average, % Na <sub>2</sub> SO <sub>4</sub>	S.D.
Compact granule	2.6, 1.9	2.2	0.4
Compact granule	2.8, 2.6	2.7	0.2
Compact granule	2.8, 2.6	2.7	0.2
Compact granule	2.9, 2.9	2.9	0.0
Compact granule	1.9, 2.8	2.3	0.6
Compact granule	4.3, 3.1	3.7	0.8
Compact granule	3.9, 3.3	3.6	0.4
Compact granule	3.3, 3.5	3.4	0.1
Compact granule	4.3, 2.6	3.5	1.2
Compact granule	5.1, 1.4	3.2	2.6
Compact granule	5.9, 5.8	5.9	0.1
Compact granule	5.1, 4.9, 1.8, 4.9, 5.5, 5.5	4.6	1.4
Compact granule	7.1, 6.2	6.7	0.6
Compact granule	7.9, 7.5, 6.8, 7.6	7.4	0.4
Compact granule	8.3, 8.8	8.6	0.4
Compact granule	8.2, 8.5	8.3	0.2
Compact granule	8.8, 8.0	8.4	0.6
Compact granule	8.3, 9.3	8.8	0.7
Compact granule	9.5, 9.5	9.5	0.0
Regular granule	13.9	13.9	
Regular granule	15.6, 15.6	15.6	0.0
Regular granule	16.9, 17.2, 17.3, 16.3, 18.1, 17.8, 16.8	17.2	0.6
Regular granule	22.1	22.1	
Regular granule	23.5, 23.5	23.5	0.0
Regular granule	24.0, 23.6	23.8	0.3
Regular granule	40.4	40.4	

CE results tend to be slightly lower than gravimetric results. The absolute difference between CE and gravimetric results ranged from 0 to 3.5% Na<sub>2</sub>SO<sub>4</sub>, and typically varied by 1.0% or less. This small difference was judged to be insignificant for our purposes.

#### 4. Conclusions

CE provides an easier and accurate means for quantitating sulfate in detergent products with equivalent results to the gravimetric procedure. The major advantages of CE are speed, simplici-

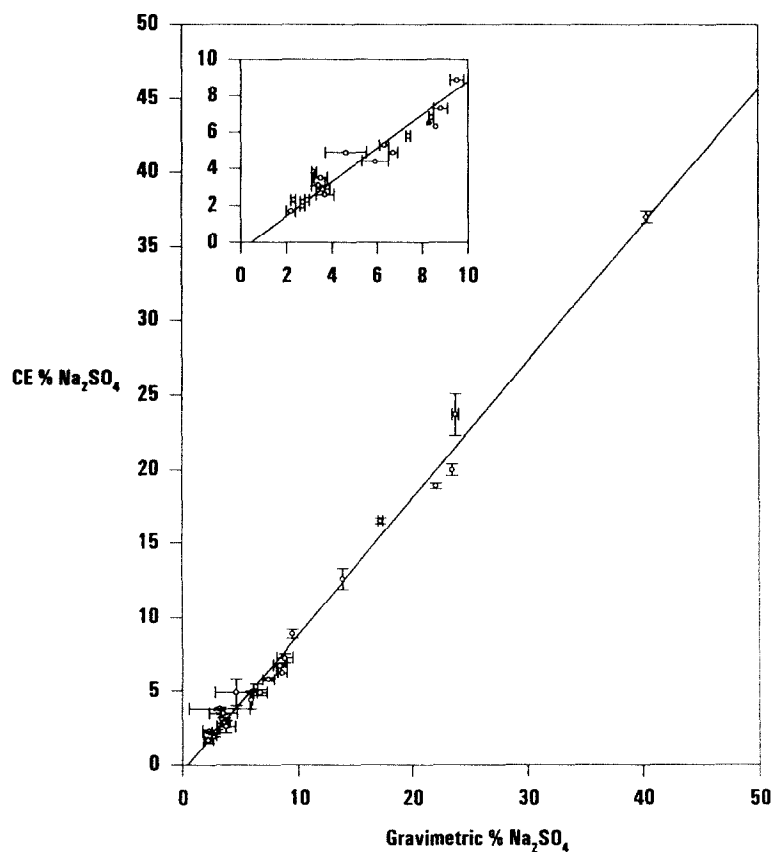


Fig. 2. Correlation plot for sulfate determinations by CE and gravimetric methods. A least squares fit of the data results in  $r^2 = 0.991$ ,  $m = 0.92 \pm 0.02$  and  $b = -0.41 \pm 0.24$  (SEE = 0.864).

Table 4

Summary of CE and gravimetric results for the determination of  $\text{Na}_2\text{SO}_4$  in seven different granular detergents and the calculated difference between methods

Sample	Gravimetric results, % $\text{Na}_2\text{SO}_4$			CE results, % $\text{Na}_2\text{SO}_4$			Difference (gravimetric - CE), % $\text{Na}_2\text{SO}_4$
	$\bar{x}$	S.D.	<i>n</i>	$\bar{x}$	S.D.	<i>n</i>	
Regular granule	17.2	0.2	7	16.5	0.1	4	0.7
Compact granule	4.6	1.4	6	4.5	1.0	3	0.1
Compact granule	7.4	0.5	4	5.8	0.1	2	1.6
Compact granule	9.5	0.0	2	8.9	0.3	2	0.6
Compact granule	3.2	2.6	2	3.8	0.1	2	-0.6
Compact granule	8.4	0.6	2	6.8	0.1	2	1.6

ty, significant time savings and minimal consumption of reagents. Because of the simplicity and speed of the CE method, duplicate samples can be easily run to check results or to get quick answers. An added benefit not discussed in the text of the paper is the potential to quantitate sulfate and chloride simultaneously by CE. Other anions such as sulfite, nitrate, orthophosphate and carbonate can also be identified in the same run, and in some cases quantitated.

## 5. References

- [1] W.R. Jones and P. Jandik, *Am. Lab.*, 22(9) (1990) 51.
- [2] W.R. Jones and P. Jandik, M. Merion and A. Weston, *US Pat.*, 5 128 005 (1992).
- [3] D.R. Salomon and J. Romano, *J. Chromatogr.*, 602 (1992) 219.
- [4] J.B. Nair and C.G. Izzo, *J. Chromatogr.*, 640 (1993) 445.
- [5] M.E. Swartz, *J. Chromatogr.*, 640 (1993) 441.
- [6] B.M. Milwidsky and D.M. Gabriel, *Detergent Analysis, A Handbook for Cost-effective Quality Control*, Halsted Press, Division of Wiley, New York, 1982.
- [7] W.W. Scott and N.H. Furman (Editor), *Standard Methods of Chemical Analysis*, Van Nostrand, Princeton, NJ, 1958.
- [8] W.R. Jones, P. Jandik and M. Merion, *US Pat.*, 5 104 506 (1992).
- [9] M.P. Harrold, M.J. Wojtusik, J. Riviello and P. Henson, *J. Chromatogr.*, 640 (1993) 463.
- [10] A.L. Heckenberg, P.G. Alden, B.J. Krol, J.P. Romano, P.E. Jackson, P. Jandik and W.R. Jones, *Waters Innovative Methods for Ion Analysis, Manual No. 22340*, Waters Division of Millipore, Milford, MA, Rev. 1.0, 1989.