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Journal of Chromatography A, 771 (1997) 155–161

JOURNAL OF CHROMATOGRAPHY A

Analysis of amine-containing phosphonates in detergent powders by anion-exchange chromatography with pulsed amperometric detection

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Received 19 November 1996; revised 7 February 1997; accepted 10 February 1997

Abstract

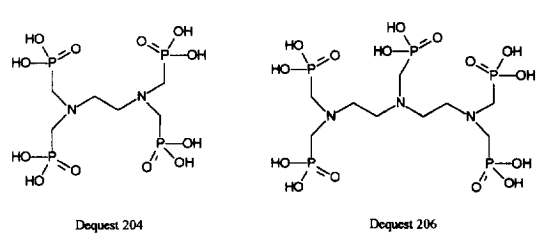
A report on an ion chromatographic method with pulsed amperometric detection (PAD) on a gold electrode is presented. The sample preparation step was extensively studied and optimized. Measurement of Dequest 204/206 in detergent powder requires a special sample pretreatment, in order to prevent oxidation of Dequest by bleach. Addition of sulphite reduces and thus inactivates the bleach. PAD is a sensitive and selective detection technique, which is applicable to amine-containing sequestrants. Concentrations of 25 mg/l (i.e., 0.5% Dequest in the detergent powder) can easily be quantitated. Other matrix compounds are completely separated from Dequest, by using gradient elution.

Keywords: Detection, LC; Pulsed amperometric detection; Phosphonates; Detergents; Dequest

1. Introduction

Polyphosphonates, such as Dequest 204 and Dequest 206, are extensively used in detergent powders as sequestering agents (Fig. 1).

Several methods of phosphonate analysis have been described in literature. Often, phosphonates are detected, after ion chromatographic (IC) separation, by post-column derivatization with Fe(III) followed by UV–Vis spectrometry [1,2]. This method suffers from large noise levels due to the mixing of reagent with eluent in the mixing coil. In addition, detection limits are too high and analysis preparation is laborious. All this results in a more complex analytical process. The method is also not specific for phosphonates.



Dequest 204 Dequest 206

Fig. 1. Molecular structures of Dequest 204 and Dequest 206.

Other post-column derivatization methods, such as the one which uses a molybdate–vanadate reagent [3], suffer from the same disadvantages as the method described above.

Also reported in literature is a method based on capillary electrophoresis, where ribonucleotides are used as electrolytes and detection is performed with indirect photometry [4]. Detection limits seem to be satisfactory in this case, but it remains unclear whether the matrix of detergent powders will disable this technique. The same applies to a method based on anion-exchange chromatography coupled to con-

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PII S0021-9673(97)00189-1

ductivity detection with ion suppression [5] where we observed a strong influence of powder matrix.

As detergent powders contain a number of anions that might interfere with the phosphonate separation a highly selective detection method is desired. An amperometric detector can meet this requirement. Dequests 204 and 206 can be selectively oxidized, because they contain amine groups. An additional advantage of the amperometric detector is its high sensitivity, which is indispensable for measuring low levels of Dequest in detergent powders.

In this paper an IC method is presented with pulsed amperometric detection (PAD) on a gold electrode. PAD employs a repeating potential versus time waveform [6–9], which in this case is a sequence of three potentials. The working potential is set to 200 mV vs. an Ag/AgCl reference electrode. At this potential, however, an oxide layer is formed and, in addition, organic material might coat and poison the gold electrode surface. Pulsing to a high positive potential oxidatively desorbs polluting organic compounds from the surface, but stimulates the formation of gold oxide. Sequential application of a high reducing potential regenerates Au from the AuO layer. Repeatedly switching from oxidizing to reducing potentials cleans the electrode and maintains an active and stable surface. The reducing potential should not be too negative, in order to prevent other chemical reductions (for example, oxygen reduction) to occur. These reactions will cause baseline disturbances during the measurement at the working potential E_1. A mild reducing potential that lasts long enough is sufficient to completely reduce the gold oxide layer [8].

The PAD technique is extensively used for the analysis of carbohydrates (HPAEC–PAD, [9,10]), for bile acids (RP-HPLC–PAD [11], HPAEC–PAD [12]) and for monoamines and diamines (IC–PAD [13]).

2. Experimental

2.1. Reagents and chemicals

Polyphosphonates, i.e., Dequest 2047 and Dequest 2066, were obtained from Monsanto (Louvain-la-Neuve, Belgium). Detergent powder samples and matrix powder, i.e., detergent powder without any Dequest, were obtained from our laboratory. 50% NaOH was purchased from J.T. Baker (Deventer, Netherlands). Sodium sulphite ($Na_2SO_3 \cdot 2H_2O$) was purchased from Merck. For all solutions Milli-Q water was used.

Eluent A consisted of pure Milli-Q water. Eluent B was prepared by degassing Milli-Q water and diluting 10.6 ml of a 50% NaOH solution to 1000 ml with Milli-Q water in a volumetric flask. The post-dose NaOH solution of 600 m*M* was prepared by diluting 31.8 ml of 50% NaOH solution to 1000 ml with Milli-Q water in a volumetric flask. All solutions were continuously degassed by helium. The standards were prepared by adding subsequently 5 ml of a 50 g/l sodium sulphite solution, the appropriate number of milliliters (usually 5–10 ml) of a Dequest stock solution and 0.5 g of detergent powder to a 100 ml volumetric flask. After addition of the powder the volumetric flask was filled and the solution was homogenized for 30 min by using a magnetic stirrer. Then the solution, with undissolved zeolite material present, was immediately filtered through a 0.22 μm Millipore filter.

Samples were prepared by adding subsequently 50 ml of a 50 g/l sodium sulphite solution and 5 g of a split powder sample to a 1000 ml volumetric flask. The solution was diluted to 1000 ml and the solution was homogenized. Immediately thereafter, a part of the solution was filtered through a 0.22 μm Millipore filter.

2.2. Instrumentation

Chromatography was performed on a Dionex HPLC system equipped with a LC30 chromatography oven, a GP40 gradient pump, an ED-40 pulsed amperometric detector with a gold working electrode, an AS40 autosampler and a 250×4 mm I.D. Dionex AS11 column protected by a 4 mm I.D. Dionex AG11 guard column.

As post-dose pump for high sodium hydroxide concentrations a Waters 510 isocratic, double head pump is used. An obsolete column is used as pulse damper.

Data are processed by Perkin-Elmer Turbochrom 4.1 <0G07> for integration and quantification.

2.3. Method of analysis

The chromatographic separation has been optimized for whole detergent powder samples. An NaOH gradient is used to separate Dequest from other powder compounds and to separate both types of Dequest.

The first part of the gradient completely retains Dequest onto the column and fully elutes other powder components. Thereafter, Dequests are separately eluted by gradually increasing the NaOH concentration. Finally, a 200 m*M* eluent is flushed through the column to clean the column of any retained material.

A quaternary gradient pump was programmed to generate the elution gradient between flask A (Milli-Q water) and flask B (200 m*M* NaOH) as described in Table 1.

The PAD system was programmed as follows: "integrated amperometry" mode; Ag/AgCl reference electrode; range: 10 nC; column oven temperature: 30°C.

The waveform used is described in Table 2:

The response of the Au electrode depends on the pH, which is changed by the NaOH gradient. The pH of the eluent in the detector is maintained at a constant value by post-dosing NaOH at the inlet of the detector. A minimum of 300 m*M* is required for the detection, whereas the gradient runs from 10–200 m*M*. Therefore, a 600 m*M* NaOH solution is added post-column at the same flow-rate as the eluent. NaOH concentrations in the detector are in the range 305–400 m*M*. In this NaOH range hardly any baseline drift is observed, certainly not during peak elution.

Separation of Dequest was performed with an eluent flow of 1 ml/min and a post-column flow (600 m*M* NaOH) of 1 ml/min. Injection volumes of standards and samples were 100 μl.

The amount of Dequest was expressed as follows: for a standard made by weighing 100 mg of Dequest as obtained by Monsanto and adding it to 5 g of

Table 2
The potential versus time waveform for PAD

Time (s)	mV	Step
0	+200	Start of the waveform (working potential)
0.27	+200	Acquisition of data
0.37	+200	at working potential
0.38	+600	Oxidation of organic pollutants
0.58	+600	from gold electrode
0.59	−150	Reduction of gold oxide which was
1.09	−150	formed during the oxidation step

Table 1
The gradient programme

Time (min)	A (pure water) (%)	B (200 m*M* NaOH) (%)	Step
0	95	5	Start of the gradient method
2.5	95	5	Injection of sample
2.5	95	5	Complete retention of Dequest while other
6.5	95	5	powder components are eluted
6.5	95	5	
14	70	30	Elution and separation of Dequest
18.5	70	30	
19.5	0	100	Cleaning of the column
24.5	0	100	
27	95	5	Back to starting conditions
40	95	5	and conditioning of the electrode

matrix powder the concentration in the powder is said to be 2%. When this sample (5 g) is dissolved in 1000 ml of Milli-Q water for analysis purposes, the concentration becomes 100 mg/l. Note that the total active acid concentration is much lower than 100 mg/l (about 33 mg/l for Dequest 2047 and 20–24 mg/l for Dequest 2066)!

3. Results and discussion

3.1. Sample preparation

3.1.1. Addition of sulphite to prevent oxidation of Dequest

In order to measure Dequest in detergent powder samples, the influence of the powder on Dequest has to be eliminated. When 5 g of detergent powder, containing both Dequest and bleach, is dissolved in 1000 ml of water no Dequest is observed in the chromatogram. The bleach system immediately oxidizes Dequest to its N-oxides after dissolution. The N-oxides are not detectable with PAD in the oxidative mode, because they already have been oxidized. To prevent the bleach system from oxidizing Dequest, sulphite is added to reduce the bleach. An eight-fold excess of sulphite with respect to TAED was found to be suitable.

Furthermore it appeared that the order of mixing sulphite, matrix powder and Dequest was of great importance. When sulphite powder was first added to detergent powder with Dequest before dissolution, irreproducible results were obtained. However, when detergent powder with Dequest was added to a sulphite solution, the reproducibility improved remarkably, probably due to the improved accessibility of sulphite to the bleach.

Additionally, a 100% recovery of Dequest is obtained. Another aspect that had to be checked is the effect of sulphite on Dequest oxidized by storage of the detergent powder. For this purpose, we dissolved Dequest in a powder solution without adding sulphite. The Dequest peaks almost completely disappeared in the chromatogram due to reaction of Dequest with bleach. After adding sulphite to this same solution Dequest peaks were still absent and did not appear again, indicating that oxidized Dequest is not reduced by sulphite. Addition of sulphite is therefore appropriate to monitor the Dequest concentration during storage.

3.1.2. Further sample preparation

For convenience standards were prepared, using Dequest stock solutions, instead of Dequest powder. The effect of using a Dequest stock solution instead of the proper amount of Dequest powder was checked and appeared to be negligible.

As the Dionex AS40 autosampler uses vials with a cap which contains a filter, samples are in general filtered just before injection. In the case of detergent powder samples, this appeared to cause problems. The time interval between dissolution of the sample and actual filtration may be quite long, especially when many samples are measured. In the non-filtered solution, reactions may still take place, which may change the concentration or status of Dequest (oxidation, complexation of other metals). Therefore, filtration of the sample or standard solution just after preparation is essential. Moreover, the mesh size of the 0.22 μm Millipore filters is much smaller than that of the filters in the caps of the vials (20 μm!).

After filtration the samples remain stable for at least two days, also when stored in the autosampler where the temperature is slightly higher than ambient.

Preparation of a standard with a Dequest 2047 concentration of 35 mg/l in six-fold yields a standard deviation of 3.0% in peak area. This value also includes variation caused by the instrument.

3.2. Sensitivity of the electrode

As the electrode is very sensitive, it is also very liable to pulses of the pump. Therefore, the post-dose pump in particular should meet some requirements. A double head pump delivers a quieter pulse than a single head pump. Furthermore, an extra pulse damper can compensate for the pulses. Use of an obsolete column is very effective.

The electrode can partly lose its sensitivity, yielding decreasing peak areas. Fouling of the gold electrode, that might occur despite the cleaning pulse procedure, causes this sudden decrease in response. Cleaning the electrode with a soft tissue to remove any dark-coloured deposit will restore the response. If the fouling is persistent, the electrode should be

cleaned with polishing powder (Al_2O_3, 1 μm) on a polishing pad.

Prior to the quantitation of samples or the measurement of calibration plots, it is advisable to perform repeated injections of the same standard to assure stable sensitivity. It appeared that the performance of the electrode is dramatically improved when the electrode is allowed to condition before each new injection. Thus, after the gradient has returned to starting conditions (95% A, 5% B, at t=27 min) the status quo is maintained until t=40 min. Only then is a new sample injected into the system.

3.3. Calibration plots

Dequest 2047 and 2066 were well separated when using the gradient as described in Table 1. Fig. 2 shows a chromatogram of Dequest 2047 and Dequest 2066 in pure water. It is clear that the Dequest material as obtained from Monsanto is not pure, as more than one peak is observed for both types of Dequest.

Fig. 3 shows a chromatogram in a detergent powder solution, containing bleach. No interference (overlapping peaks) of matrix compounds is observed, but a large peak is appearing at the beginning of the chromatogram. This peak also contains the excess of sulphite.

Slope (in peak area units per mg/l) and intercept (in peak area units) of the linear calibration lines are respectively 17.52±0.87 and 162.8±6.28 for Dequest 2047 (range 0–50 mg/l) and 74.63±5.76 and −491.6±82.4 for Dequest 2066 (range 50–100 mg/l), based on a 95% confidence interval for five observations per calibration line. The correlation coefficients are 0.999275 and 0.998231 for Dequest 2047 and Dequest 2066, respectively.

As the calibration plots are linear and standards are prepared in exactly the same way as the detergent powder samples, accurate quantitation of Dequest levels is possible.

If other components are present in a specific

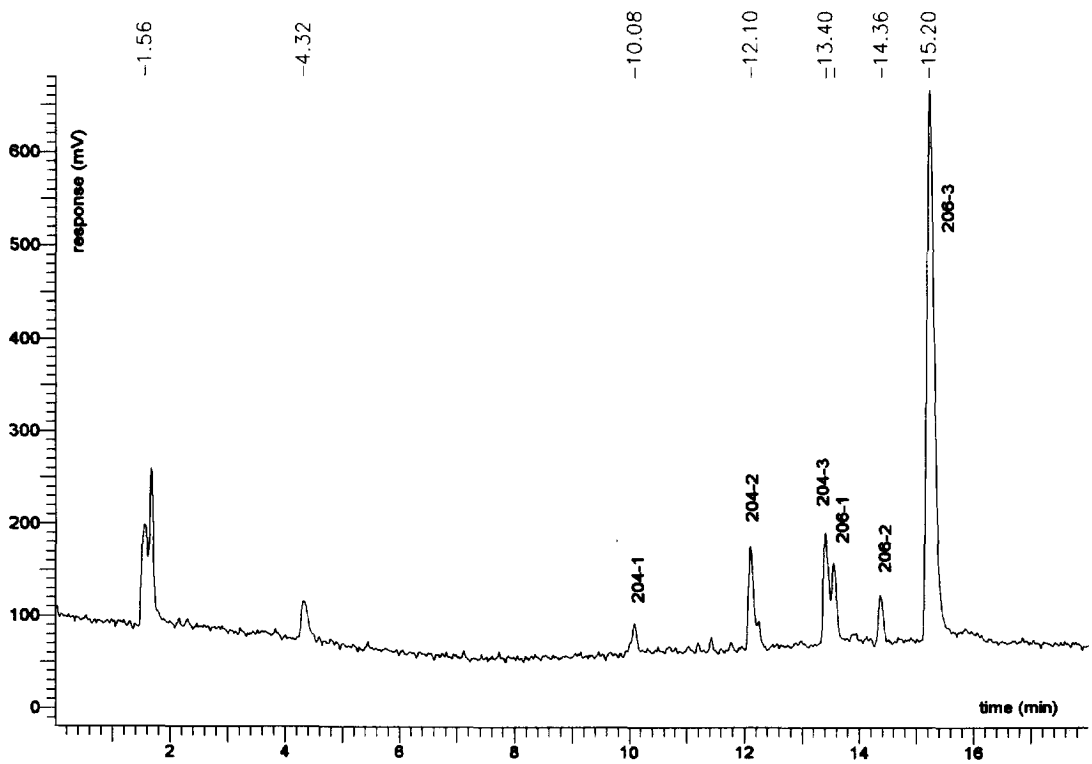

Fig. 2. Chromatogram of a mixture of Dequest 204 (50 mg/l) and Dequest 206 (100 mg/l) in pure water.

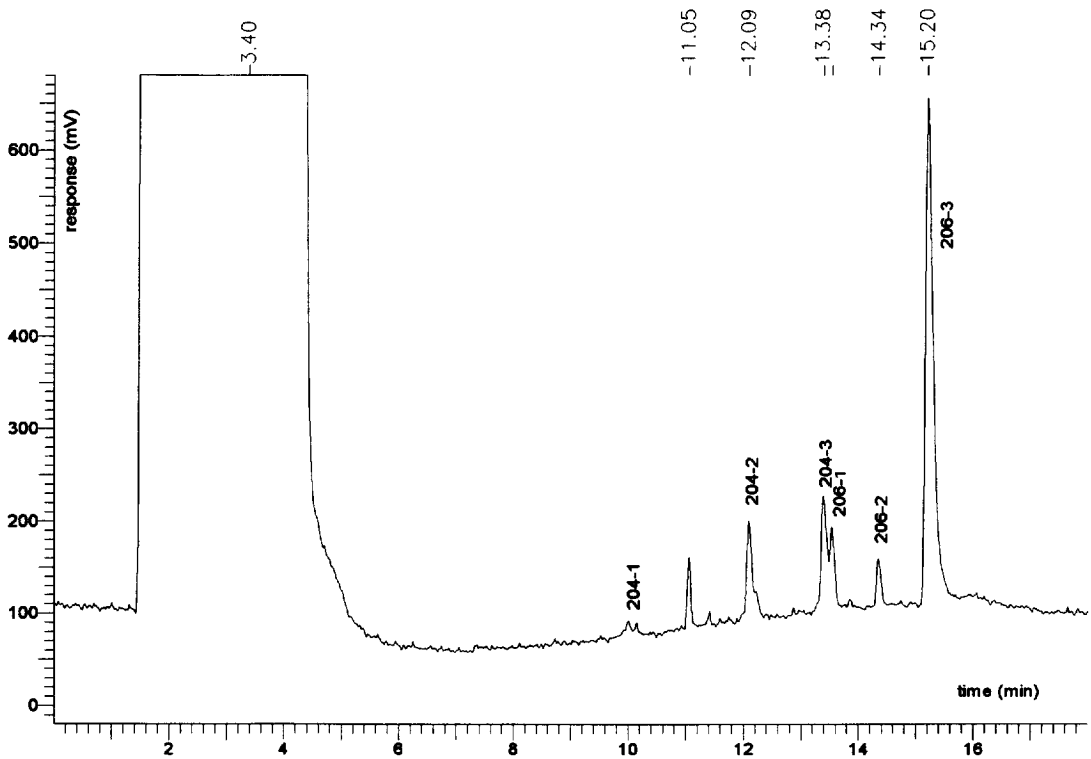

Fig. 3. Chromatogram of Dequest 204 (50 mg/l) and Dequest 206 (100 mg/l) in detergent powder.

sample which give overlapping peaks with the Dequest peaks, the NaOH gradient should be adapted. In general, better separation is obtained by extending the "elution and separation of Dequest" step (see Table 1).

4. Conclusions

A selective and sensitive method is available to measure low concentrations of Dequest in detergent powders. However, the robustness of the method might still be improved. Accurate preparation of the samples, careful usage of the PAD and optimal conditions for the electrode of the PAD are essential to obtain standard deviations better than 3%.

The within-day reliability of the method can be checked by repeated injection of a freshly prepared standard. Between-day variations of the sensitivity occur when the detector had been switched off. This should be corrected by remeasuring the calibration line.

Dequest stock solutions, standards and samples can be prepared at least one week before measuring (and probably more), so that sample and standard preparation can be efficiently carried out.

The method is also applicable to other sequestrants which contain amine groups.

Acknowledgments

The authors wish to acknowledge Mrs. H.M. Haasnoot-Aalvanger for her experimental contribution.

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