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Journal of Chromatography A, 920 (2001) 247–253

JOURNAL OF CHROMATOGRAPHY A

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Analysis of fountain solutions for anionic components, including alkylbenzenesulfonates, carboxylates and polyphosphates, by a combination of ion-exchange and ion-exclusion chromatography and inductively coupled plasma atomic emission spectrometry

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Abstract

A method for the quantitative determination of the major anionic constituents of fountain solutions, typically mono-, di- and hydroxycarboxylates, alkylbenzenesulfonates, and inorganic anions, including orthophosphate and polyphosphates, is presented here for the first time. The analytical problems arising from extensive co-elution of many of these analytes on an ion-exchange column have been resolved through a combination of (i) careful selection of the concentration gradient of the sodium hydroxide eluent; (ii) parallel analysis by ion-exclusion chromatography; and (iii) determination of total phosphorus by inductively coupled plasma atomic emission spectrometry.

Keywords: Fountain solutions; Alkylbenzenesulfonates; Carboxylic acids; Polyphosphates; Inorganic anions; Organosulfur compounds

1. Introduction

Fountain solutions (or founts) are aqueous solutions used extensively in the printing industry to optimise the lithographic printing process. There are a wide variety of compositions of fountain solutions to suit differing printing applications, ranging from newspapers and magazines to food packaging. In addition, variations in formulations exist for differences in regional supply water quality. The components typically added to fountain solutions include mono-, di- and hydroxycarboxylates, alkylbenzenesulfonates, orthophosphate and polyphosphates. Quantitative analysis of the anionic components of fountain solutions is important for quality control purposes as many are used in the control of pH, surface tension and lithographic plate non-image hydrophilicity. The toxicity of some of the anionic components [1,2] means that their quantitative analysis is also important to monitor or assure compliance with environmental regulations and legislation. The ionic nature of many of these compounds suggests that ion chromatography may be a useful tool for their analysis, indeed many workers have reported the use of chromatographic and other techniques for the analysis of carboxylates [3–9], alkylbenzenesulfonates [2,7–14] and polyphosphates [15–20] in a variety of aqueous and non-aqueous media.

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0021-9673/01/$ – see front matter
PII: S0021-9673(01)00553-2

There also exist a number of studies of chromatographic separation of solutions containing both carboxylates and alkylbenzenesulfonates but these have largely focussed on alkylbenzenesulfonates and their aromatic carboxylate biodegradation products [7–9] rather than the aliphatic carboxylates typically found in fountain solutions. Despite extensive searches we are not aware of any previously published chromatography studies applied to fountain solutions. Fountain solutions can present particular analytical problems, notably the extensive co-elution of the various anionic components on ion-exchange columns and the instability of polyphosphates [16,18]. In this paper, we present procedures developed to resolve these difficulties. The procedures involve the combined use of ion-exchange and ion-exclusion chromatography [21] and of inductively coupled atomic emission spectrometry (ICP–AES).

2. Experimental

2.1. Apparatus

Ion-exchange chromatography was performed with a Dionex 4000i gradient ion-exchange system (Dionex, Sunnyvale, CA, USA). This system comprised a Dionex IonPac AG11 guard column, an AS11 analytical column, and an anion self-regenerating suppressor (ASRS) to remove the sodium hydroxide eluent post-column before introduction into an electrical conductivity detector. Samples (50 μl) were injected automatically with a Dionex autosampler.

Ion-exclusion chromatography was carried out using a Dionex QIC isocratic ion-exclusion system with a Dionex IonPac ICE–AS1 column. The octanesulfonic acid eluent was suppressed post-column with 10 m*M* tetrabutylammonium hydroxide using a Dionex Autoregen system before introduction into an electrical conductivity detector. Samples (50 μl) were injected manually.

Total phosphorus and total sulfur were determined on an Horizon ICP–AES system (VG Elemental, Winsford, UK) using the atomic emission lines at 213.618 nm and 182.037 nm, respectively.

2.2. Reagents and samples

Sodium hydroxide (50%) was purchased from Merck/BDH (Poole, UK) and used to produce the 1.5 m*M* and 200 m*M* NaOH eluents for the ion-exchange system. Octanesulfonic acid (OSA; 0.1 *M*) was purchased from Dionex (Camberley, UK). Tetrabutylammonium hydroxide (TBAOH; 40% solution) was purchased from Sigma–Aldrich (Poole, UK). Standards for chloride, nitrate, sulfate and orthophosphate were prepared from ''AnalaR'' grade potassium chloride, ammonium nitrate, potassium sulfate and potassium dihydrogenorthophosphate, respectively, from Merck/BDH. Calibration standards for tripolyphosphate as well as the alkybenzenesulfonates and carboxylic acids were supplied by Varn Products (Irlam, Greater Manchester, UK). All calibration standards were prepared fresh every day prior to analysis.

The accuracy of prepared calibration standards used on the ion-exchange system was checked against a certified standard solution (ICMIX1-100) purchased from Glen Spectra (Stanmore, UK). ICMIX1-100 contained chloride, nitrate, sulfate and orthophosphate at concentrations of 30.00, 100.00, 150.00 and 148.4 mg/l, respectively. Five separate ten-fold dilutions of the Glen Spectra calibration solution were prepared and analysed on the ion-exchange system calibrated with a standard solution prepared in our laboratory. The agreement was found to be better than 5% for chloride and better than 2% for nitrate, sulfate and orthophosphate.

The calibration standards used for ICP–AES analysis were obtained by serial dilution of a 1000 mg/l mixed element standard purchased from Johnson Matthey (Royston, UK).

All dilutions were carried out using 18 MΩ deionised water obtained using a ELGA Maxima System (USF Elga, High Wycombe, UK).

Fountain solutions from a variety of sources were provided by Varn Products. These were typically diluted 250-fold and 2000-fold in order to achieve a reasonably close match between the concentrations of analytes in the samples with those in the calibration solutions used. For the ion chromatography, occasional further dilutions were required, particularly in order to reduce over-range peaks. Some of the fountain solutions tended to separate into immis-

cible phases on standing and so were shaken immediately prior to analysis. To prevent contamination of the columns alcohols and aromatics might normally be removed before injection, however we found no need to adopt such precautions for the samples we analysed, in part, because of the large dilution factors used.

2.3. Quantitation

Peak integration and data management for the ion-exchange and ion-exclusion systems was carried out using Dionex Peaknet software. Quantitation was achieved through the comparison of integrated peak areas for samples with closely matched calibration standards (Figs. 1 and 2) after suitable corrections for peak overlap as detailed below. Ion-exchange chromatographic performance was monitored by observing the peak shapes and retention times for orthophosphate and tripolyphosphate, these being particularly sensitive to metal contamination (from sources other than fountain solutions) on the column as well as changes in stock eluent concentrations associated with eluent aging [16]. Quantitation of total phosphorus and total sulfur was carried out using 3 point calibrations.

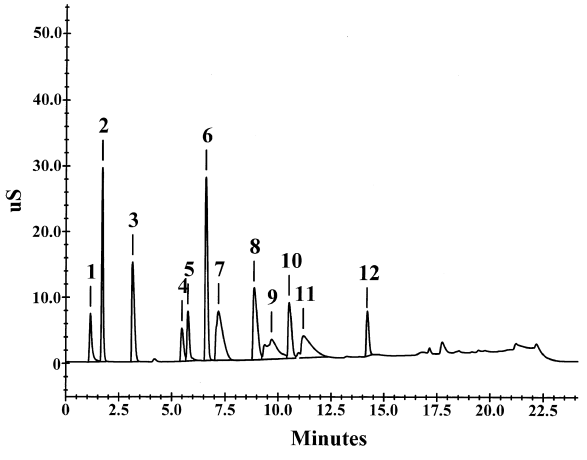

Fig. 1. Ion-exchange chromatogram of a calibration standard containing alkylbenzenesulfonates, carboxylates, phosphates and other inorganic anions typically found in fountain solutions. Column: IonPac AS11 (250 mm×4 mm I.D.); mobile phase: sodium hydroxide, 0–2 min isocratic; 2–10 min, gradient 4.5 m*M* to 30.5 m*M*, 10–20 min, gradient 30.5 m*M*–80.2 m*M*, 20–30 min, gradient 80.2 m*M*–4.5 m*M*; flow-rate 1.8 ml/min. Volume injected 50 μl; Detection: electrical conductivity; peak identification: 1=acetate (0.25 μg), 2=chloride (0.20 μg), 3=nitrate 0.25 μg), 4=glutarate (0.25 μg), 5=malate 0.25 μg), 6=sulfate (0.25 μg), 7=toluene sulfonate (1.5 μg), 8=orthophosphate (0.50 μg), 9=xylene sulfonate (1.0 μg), 10=citrate (0.50 μg), 11=cumene sulfonate (1.25 μg), 12=tripolyphosphate (2.0 μg).

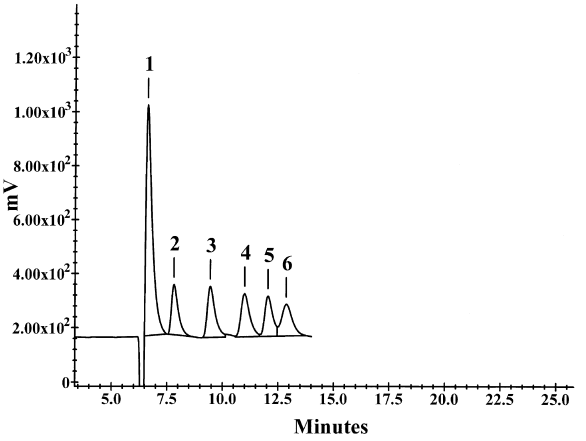

Fig. 2. Ion-exclusion chromatogram of calibration standard containing orthophosphate and carboxylates typically found in fountain solutions. Column: IonPac ICE–AS1 (250 mm×9 mm I.D.); mobile phase: 1 m*M* octanesulfonic acid; flow-rate 1.0 ml/min. Volume injected 50 μl; detection: electrical conductivity; peak identification: 1=orthophosphate (2.5 μg), 2=malate (0.50 μg), 3=succinate (0.50 μg), 4=glutarate (0.50 μg), 5=acetate (0.50 μg), 6=adipate (0.50 μg).

3. Results and discussion

3.1. Separation and optimisation of chromatographic parameters

It was found during the analysis of synthetic calibration standards and fountain solutions that the co-elution on the ion-exchange system of orthophosphate with xylene sulfonate and of citrate with cumene sulfonate was particularly sensitive to the eluent gradient. Resolution of both sets of peaks could be achieved by careful selection of an appropriate gradient. For the chromatographic conditions applicable to Fig. 3, increasing the elution gradient over the time period 2 to 10 min from 1.88 m*M*/min (Fig. 3a) to 4.00 m*M*/min (Fig. 3c) reverses the order of elution of orthophosphate and xylene sulfonate and also reverses the order of elution of citrate

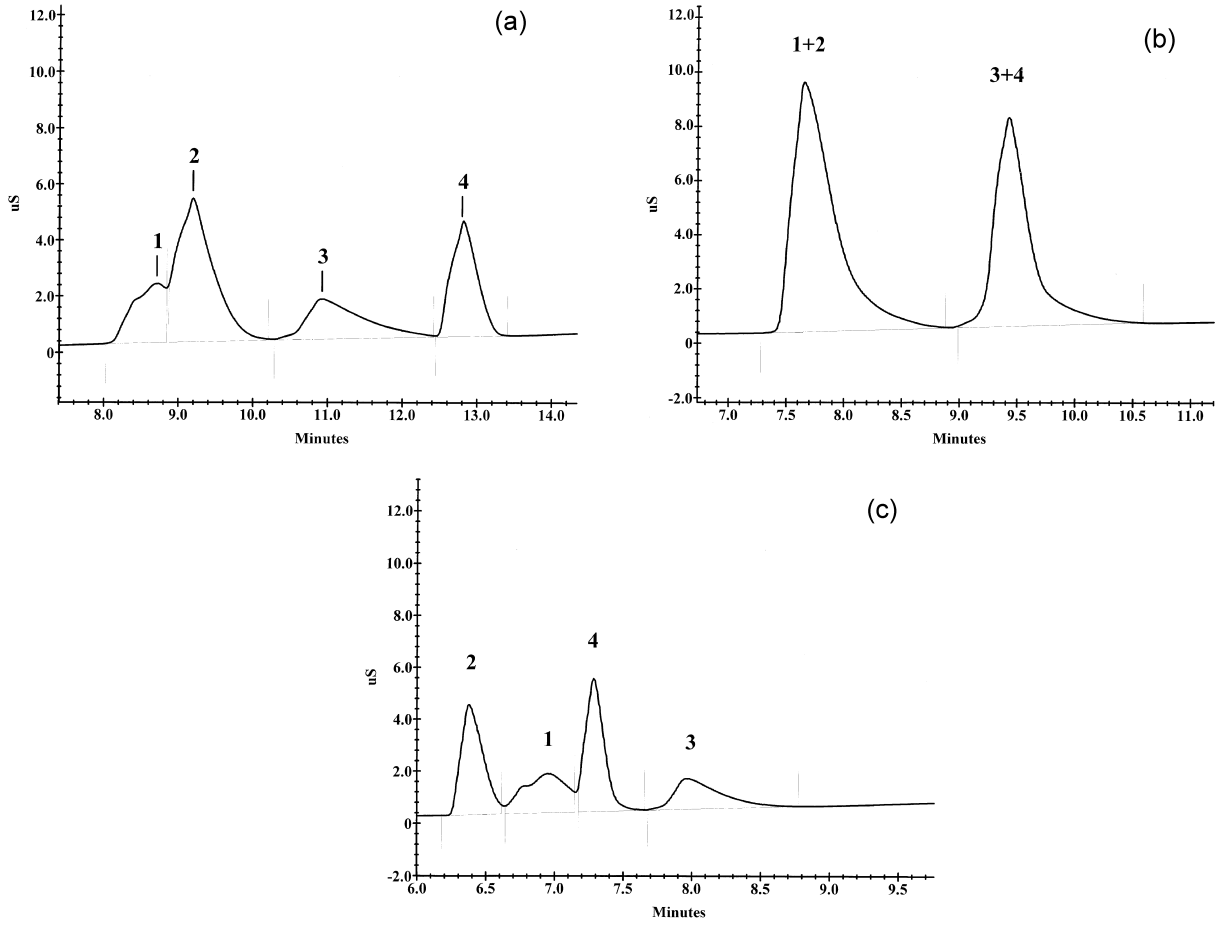

Fig. 3. Ion-exchange chromatograms illustrating the sensitivity of elution order to eluent gradient. The chromatographic conditions were as for Fig. 1 except that that sodium hydroxide concentration gradients were as follows: (a) 0 –2 min, isocratic 2 m*M*, 2–10 min, gradient 2 m*M*–9 m*M*, 10–20 min, gradient 9 m*M*–31 m*M*; (b) 0–2 min, isocratic 2 m*M*, 2–10 min, gradient 2 m*M*–17 m*M*, 10–20 min, gradient 17 m*M*–39 m*M*; (c) 0–2 min, isocratic 2 m*M*, 2–10 min, gradient 2–35 m*M*, 10–20 min, gradient 35 m*M*–45 m*M*. Peak identification: 1=xylene sulfonate (0.50 μg), 2=orthophosphate (0.50 μg), 3=citrate (0.50 μg), 4=cumene sulfonate (0.50 μg).

and cumene sulfonate, whilst at an intermediate elution gradient of 2.75 m*M*/min (Fig. 3b) orthophosphate and xylene sulfonate co-elute as do citrate and cumene sulfonate. The optimum eluent gradient over the time period 2 to 10 min for separating these two pairs of analytes was found to be 3.50 to 4.00 m*M*/min.

Optimisation of the ion-exchange chromatographic parameters to separate alkylbenzensulfonates from carboxylates and orthophosphate resulted in conditions under which co-elution of malate, gluturate, succinate and adipate occurred as well as co-elution of acetate and glycolate. The ion-exclusion chromatographic system, however, is well suited to separate these carboxylates [4,5,21] (Fig. 2) and provided the basis for unambiguously interpreting the co-eluting peaks from the ion-exchange system.

Tripolyphosphate was observed in the ion-exchange system as either a single late-eluting peak or as a series of late-eluting peaks, the latter being

particularly difficult to quantify in the absence of unambiguous identification of the breakdown products.

3.2. Scheme for integration of chromatographic and ICP–AES data

On the basis of the observed separations, the following scheme was developed to integrate the ion-exchange, ion-exclusion and ICP–AES data to calculate the concentrations of carboxylate, alkylbenzenesulfonate and inorganic anions in fountain solutions (Fig. 4). Simple inorganic anions, citrate and the alkybenzenesulfonates, toluene sulfonate, xylene sulfonate and cumene sulfonate, are determined by ion-exchange chromatography using an appropriate elution gradient to eliminate peak overlap between (i) orthophosphate and xylene sulfonate and (ii) citrate and cumene sulfonate (Fig. 1). No attempt was made to quantify the relative concentrations of the isomers of xylene sulfonate. Malate, glutarate, acetate and adipate are determined by ion-exclusion chromatography (Fig. 2). The observed co-elution of acetate and glycolate on the ion-exchange system but not on the ion-exclusion system means that glycolate may be quantified from the integrated area of the acetate ion-exchange system peak not accountable by the known concentration of acetate determined by the ion-exclusion system. Determination of glycolate by this procedure enables its contribution to the combined succinate+glycolate ion-exclusion system peak to be determined and hence the concentration of succinate to be quantified. Tripolyphosphate is calculated from the difference between the total phosphorus determined by ICP–AES and that contributed by orthophosphate.

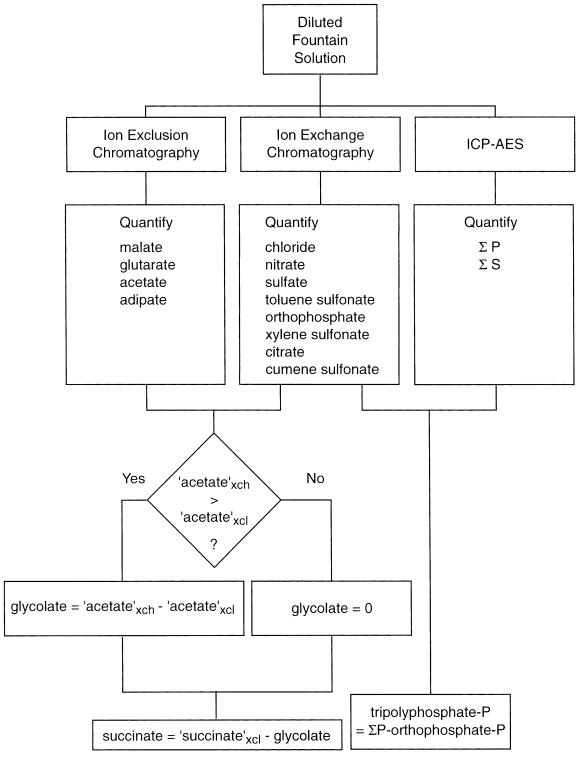

Fig. 4. Scheme for quantitation of alkylbenzenesulfonates, carboxylates, tripolyphoshate and simple inorganic anions in fountain solutions by parallel ion-exchange chromatography, ion-exclusion chromatography and ICP–AES. The subscripts ''xch'' and ''xcl'' refer to the ion-exchange and the ion-exclusion system respectively. ΣP refers to total dissolved phosphorus.

3.3. Accuracy

The accuracy of the instrumental analysis and data reduction protocol was assessed by the analysis, as unknowns, of mixed component standards and by the comparison of total sulfur obtained by ICP–AES and that calculated from the concentrations, determined by combined ion-exchange and ion-exclusion chromatography, of individual sulfur-bearing species.

Analysis of solutions spiked with mixed alkybenzenesulfonates, with concentrations of individual analytes (toluene sulfonate, xylene sulfonate and cumene sulfonate) between 3.75 and 60 mg/l, resulted in recoveries between 86 and 104%, with lowest recoveries obtained for the lowest concentration solutions. Analysis of solutions spiked with carboxylate standards, with concentrations of individual analytes of 10 mg/l, resulted in recoveries between 99 and 102%. Analysis of solutions spiked with a mixture of alkylbenzenesulfonates, carboxylates, polyphosphates, orthophosphate, chloride, nitrate and sulfate, with concentrations of individual analytes between 5 and 50 mg/l, resulted in recoveries of between 98 and 108%, the worst re-

coveries being obtained for malate and cumene sulfonate.

The agreement between the concentration of sulfur obtained by ICP–AES and that calculated from the sum of the concentrations, determined by chromatography, of sulfate and the various observed alkybenzenesulfonates was better than 20 % for all solutions analysed. There was broad agreement between the concentrations of tripolyphosphate calculated from the concentrations of orthophosphate and total phosphorus and directly from ion-exchange chromatography, provided that no other phosphorus species were present. The former calculations are considered more reliable where more than one polyphosphate peak in the ion-exchange system is observed because of uncertainties in the variation of analytical sensitivity for the various peaks.

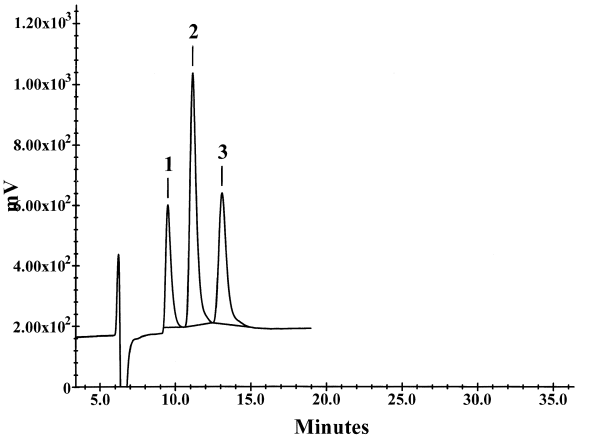

Fig. 6. Ion-exclusion chromatogram of an unknown fountain solution. Sample and dilution same as for Fig. 5. Chromatographic conditions same as for Fig. 2. Peak identification: 1=glycolate, 2=glutarate, 3=adipate.

3.4. Analysis of fountain solutions

Examples of chromatograms of an unknown fountain solution obtained are shown in Figs. 5 and 6. Tripolyphosphate breakdown products can be seen as the small late-eluting peaks on Fig. 5. It can be clearly seen that glutarate and adipate co-elute on the ion-exchange system but are clearly resolved by ion-exclusion chromatography. Commercial confidentiality means that we are unable to present the analyses of all the individual solutions, but the range and mean of the various analytes found in the sample set as whole are summarised in Table 1.

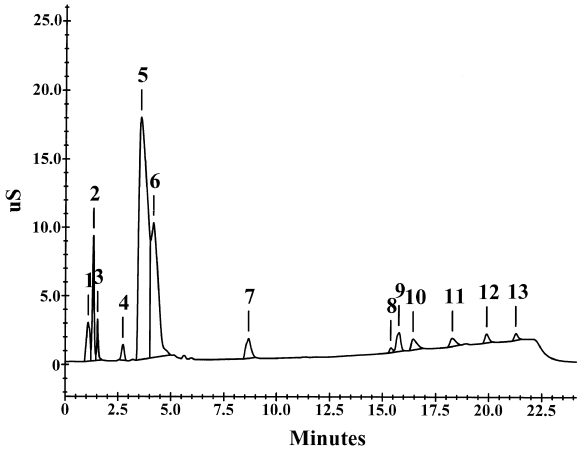

Fig. 5. Ion-exchange chromatogram of an unknown fountain solution, diluted 250 fold. Chromatographic conditions were as for Fig. 1. Peak identification: 1=glycolate, 2=chloride, 3=unknown, 4=nitrate, 5=glutarate, 6=adipate, 7=orthophosphate, 8–13=tripolyphosphate.

4. Conclusions

A scheme, integrating data from ion-exchange chromatography, ion-exclusion chromatography and ICP–AES, has been developed in this study to quantify the major anionic components in fountain solutions. The scheme may be used to unambiguously determine the concentrations of carboxylates (acetate, malate, succinate, glutarate, adipate, citrate and glycolate) alkylbenzenesulfonates (xylene sulfonate and cumene sulfonate) and inorganic anions (chloride, sulfate, nitrate, orthophosphate and tripolyphosphate). The analytical methodology potentially has additional application in the determination of corrosion and scale inhibitors and related species in the chemical and petroleum industries.

Table 1
Maximum and mean concentrations of anionic components quantified in 15 fountain solutions by a combination of ion-exchange chromatography, ion-exclusion chromatography and ICP–AES using the scheme in Fig. 4. Mean concentrations refer only to the set of samples for which a given component was detected

Anionic component	Number of fountain solutions in which component was detected	Maximum concentration found (mg/l)	Mean concentration found (mg/l)
Xylene sulfonate	5	89 000±5000	34 000
Cumene sulfonate	2	62 000±6000	52 000
Acetate	9	26 000±1000	12 000
Malate	7	9800±1000	5600
Succinate	4	11 000±600	4300
Glutarate	4	15 400±800	7400
Adipate	3	11 200±600	5100
Citrate	10	105 000±6000	23 000
Glycolate	2	9600±600	6200
Chloride	4	870±30	420
Nitrate	10	26 300±800	11 000
Sulfate	9	740±30	420
Orthophosphate	13	26 000±1000	10 000
Tripolyphosphate	6	14 400±2000	7700

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