The Analyst

Perspective

Stability of bromate species immobilised on microcolumns of activated alumina†

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Microcolumns of activated alumina (*n* = 30) were charged with bromate standard solution (0.5 ml, 6.0 μg l^{-1}) and stored at 4 °C in a light-tight container. Microcolumns were removed at regular time intervals (1 h, 2 and 3 d and 1, 2, 3, 4 and 8 weeks) and bromate species were eluted and quantified by flow-injection ICP-MS. Analyte recoveries were found to be quantitative (96–101%) and reproducible over the 8 week period. These results indicate that for trace level determinations (μg l^{-1}) of bromate, a microcolumn format may provide a convenient and reliable route for delivery of external calibrants and reference materials.

Keywords: *Bromate; stability; activated alumina microcolumns; water; inductively coupled plasma mass spectrometry*

Carcinogenic by-products (*e.g.*, trihalomethanes) may be generated as a result of deploying traditional drinking water disinfection processes such as chlorination, hence the considerable interest in developing alternative water treatments such as ozonation. However, ozonolysis of bromide-containing waters may result in bromate formation,[1–3] which is itself a possible human carcinogen.[4] The US EPA, the EC and the WHO have recommended a maximum contamination level (MCL) of 10 μg l^{-1} bromate in drinking waters.[5] This limit has been defined primarily on the detection capability of existing ion chromatographic methodologies[5–8] and not on toxicological considerations (the target concentration level of bromate in drinking waters is zero), hence the need for more sensitive and/or alternative analytical techniques.[9,10]

Koudjonou *et al.*[7] used conductimetric detection within anion suppression ion chromatography and established a detection limit for bromate of 2 μg l^{-1}. This study, however, incorporated a preconcentration step, which extended the analysis time (10 min) and also resulted in a relatively poor precision (RSD = 10%). Alternative analytical techniques are available for bromate determination, including an indirect flow injection (FI) spectrophotometric procedure based on the oxidation of chlorpromazine by bromate.[10] The limit of detection is 0.8 μg l^{-1}, but the method is susceptible to interference caused by the presence of co-existing oxidants in natural waters. Recently, Creed *et al.*[11] interfaced ion chromatography with inductively coupled plasma mass spectrometry (ICP-MS). A limit of detection of 0.1 μg l^{-1} for bromate was realised with a typical run time of 10–20 min. An FI system with alumina microcolumns has also been interfaced with ICP-MS and used to determine ultra-trace levels of bromate in drinking waters.[12] In this approach, the ion-exchange properties of activated alumina were used to effect the on-line preconcentration of bromate and rejection of any co-existing bromide (potential interference).

As evidenced in the recent literature, including the aforementioned FI–ICP-MS study, microcolumn technology is becoming an increasingly important trend in ultra-trace investigations.[13] Moreover, in Hg and Cr speciation studies,[14,15] analyte-enriched microcolumns have been shown to offer a convenient route to instrument calibration and development as a new reference material (RM) format. With the latter in mind and given the urgent need to validate new methods for the determination of bromate in process and drinking waters, a batch of microcolumns was prepared and analysed over an 8 week period in order to assess stability.

Experimental

Reagents and materials

Activated alumina (Brockman Grade I, particle size 150–180 μm; BDH, Poole, Dorset, UK) was used for column packing. Nitric acid (0.01 M) was prepared by appropriate dilution of high purity nitric acid (UpA; Romil, Waterbeach, Cambs., UK). Ammonia solution (2 M) was prepared by diluting a high purity solution (UpA; Romil). Bromate working standard solutions were prepared by dilution of a stock standard solution of sodium bromate (1000 mg l^{-1} as Br) (Fluka, Buchs, Switzerland). All preparations were made using ultrapure, de-ionised water (MIlli-Q, Millipore, Molsheim, France).

Microcolumn preparation and immobilisation of bromate

Microcolumns (30) were prepared by packing PTFE tubes (3 cm × 1.5 mm id) with activated alumina (approximately 0.05 g). The columns were cleaned by inserting them, three at a time, in an off-line three-channel FI system with an acidic carrier stream (0.01 M HNO_3, continuous) followed by three injections of eluent (2 M ammonia solution). The microcolumns were then charged with bromate (0.5 ml, 6.0 μg l^{-1}) followed by 1 ml of nitric acid carrier and then disconnected. The enriched microcolumns were placed in polyethylene bags in a light-tight container and stored at 4 °C until analysis.

Instrumentation and quantitation

The FI–ICP-MS system, illustrated in Fig. 1, consisted of a Minipuls peristaltic pump (Gilson, Villiers-le-Bel, France), a rotary injection valve (sample injection volume 0.5 ml)

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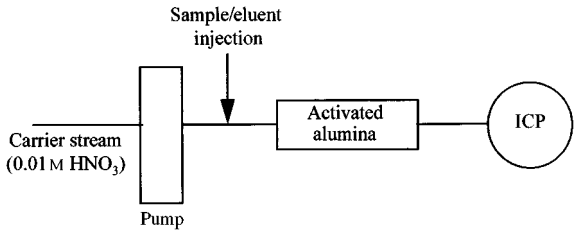

Fig. 1 Flow-injection ICP-MS system.

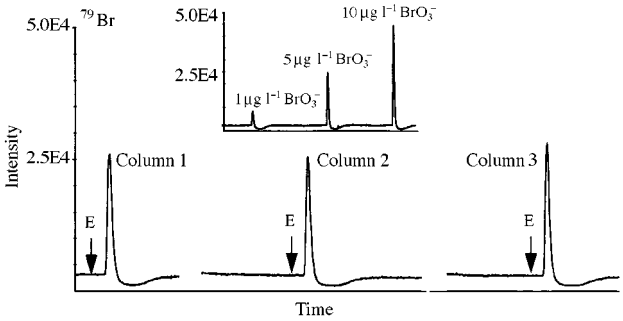

Fig. 2 Typical elutions of three enriched microcolumns (8 weeks) and a typical ion time response of signal as a function of bromate concentration.

(Omnifit, London, UK) and an HP-4500 inductively coupled plasma mass spectrometer (Hewlett-Packard, Avondale, PA, USA). The ICP-MS system was operated in accordance with the manufacturer's recommended procedures. Bromine was monitored, in the time resolved analysis mode, at *m*/*z* 97 with an integration time of 1.0 s. Bromate working standard solutions (0, 1.0, 5.0 and 10.0 μg l^{-1}) were freshly prepared, on the day of analysis, from the stock standard solution (1000 mg l^{-1} Br) and calibration was based on processing the standards in the FI system in a manner similar to that for the charged microcolumns, *i.e.*, analyte deposition (0.5 ml, 2 M ammonia solution). The response graphs obtained throughout the 8 week period exhibited good linearity (typical calibration response defined by $y = 34975x + 3742.6$; correlation coefficient 0.99907). For analysis, charged microcolumns were inserted, one at a time, into the FI–ICP-MS system at the specified time periods. Elution of immobilised bromate species was effected by a single injection of 2 M ammonia solution (0.5 ml) and the peak areas of the resulting transient signals were registered and evaluated by reference to the appropriate calibration graph. Instrument stability was checked by injection of bromate standard solutions (0, 1.0, 5.0 and 10.0 μg l^{-1}) before and after the elution of the enriched microcolumns.

Results and discussion

In a previous study,[12] bromate was shown to undergo reproducible deposition/elution on activated alumina and this behaviour was exploited in new FI–ICP-MS methodology for ultra-trace analysis of drinking waters. The main aim of this work was to extend these investigations and ascertain whether or not the immobilised species could be recovered from the column support after extended storage. If so, then there would be good prospects for preparing new external calibrants/reference materials in microcolumn format.

Typical transient responses corresponding to elution of bromate and ICP-MS detection are presented in Fig. 2 and analytical data for the complete study are summarised in Table 1. It is clear from these results that the column to column variability is low and that analyte recoveries are essentially quantitative, with good precision (short-term, RSD 0.9–5.3%; long-term, RSD 3.3%) for the 4 week period. For analysis at 8 weeks positive bias was detected although the elevated recovery was probably due to error in the ICP-MS measurement, *e.g.*, instrument drift, and not related to microcolumn storage and elution efficiency. It is concluded, therefore, that microcolumns of activated alumina provide a useful support for stabilising bromate and as such provide a simple and convenient vehicle for the delivery of precise quantities of the chemical at the trace and ultra-trace level. Further work is needed to assess the usefulness of this approach for quality control purposes in both laboratory and plant situations.

Table 1 Determination of bromate in charged microcolumns. Uncertainties, ± *s*. For experimental details, see text

Storage time	Bromate concentration/ μg l^{-1}	RSD(%)	Calibration graph correlation coefficient
1 h	5.83 ± 0.22	3.81	0.99908
1 d	5.76 ± 0.19	3.41	0.99908
3 d	6.09 ± 0.16	2.56	0.99988
1 weeks	6.16 ± 0.16	2.55	0.99986
2 weeks	6.00 ± 0.22	3.63	0.99997
3 weeks	6.34 ± 0.06	0.90	0.99996
4 weeks	5.99 ± 0.31	5.25	0.99997
8 weeks	6.86 ± 0.13	1.96	0.99940

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