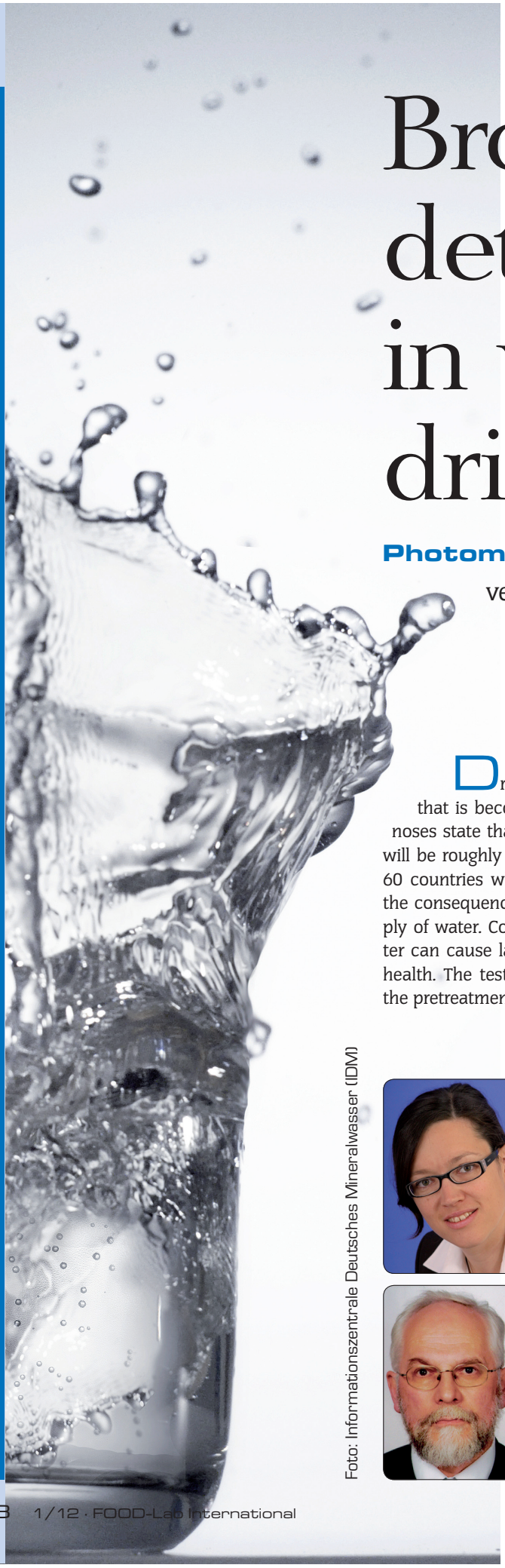

Foto: Informationszentrale Deutsches Mineralwasser (IDM)

Bromate determination in water and drinking water

Photometric determination versus ion chromatography

Drinking water is a good that is becoming ever scarcer: prognoses state that by the year 2050 there will be roughly 7 billion people in about 60 countries who will be suffering from the consequences of an insufficient supply of water. Contaminated drinking water can cause lasting damage to human health. The testing of water quality and the pretreatment of (contaminated) water supplies is thus a matter of utmost urgency. Besides purifying water by means of mechanical measures – as may be the case, for example, with surface water – disinfection also plays an essential role in ensuring the supply of clean drinking water. Bromate can arise as a by-product of the ozonation of bromide-containing water depending on the conditions (pH, temperature, duration …) prevalent at the treatment site. On account of the swift disinfection result that it provides, however, ozonation is still a method preferentially used in the treatment of water. Since bromate has a potentially carcinogenic effect when ingested orally, a limit of 0.01 mg/L has been set in the currently applicable drinking-water regulations. The determination of the concentration of bromate is correspondingly a prerequisite measure for the elimination of risks for consumers' health.

The bromate concentration in drinking water can be determined, for example, by means of ion chromatography in conjunction with conductivity measurement. This method is described inter alia in ISO 15061:2001, which is also a constituent part of the "German standard method for water, wastewater, and sludge inves-

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tigation". Depending on the approach selected, however, the ion-chromatographic method can involve the problem of the co-elution (trace/matrix problem) of bromate with e.g. chloride, which must be circumvented by the use of special separation techniques (high-capacity anion exchangers) or by special sample pretreatment. Furthermore, the measurement may be made using LC/ICP-MS. An alternative to this method is that of photometry, and this is described in the following.

Tracking down contaminants in water

The Merck company has many years of experience in the field of test kits for water and food analysis, and offers a broad spectrum of both semiquantitative rapid tests as well as reagent and cell tests for photometry. All in all the range of photometric test kits comprises roughly 150 products, including tests for about 60 different parameters. The product portfolio is rounded off by the provision of the appropriate analytical instruments, e.g. the Spectroquant® Pharo® spectrophotometer range. Applications for many other parameters are available on request, enabling customers to perform their own analyses even without a special test kit.

Determining bromate: photometry versus ion chromatography

Anyone wishing to measure the bromate content of water but who does not possess the necessary ion-chromatography equipment can turn to the photometric principle. The method is based on the reaction of 3,3'-dimethylnaphthidine with iodide and bromate that produces a red radical cation, the absorbance of which is then determined photometrically. The more bromate there is present in the sample, the more intensive the color of the solution at the end of the reaction time.

Before the concentration can be determined, the user must first record an own calibration curve, on the basis of which the absorbances measured in unknown samples are then converted into concentration results. The instruments supplied by Merck with their preprogrammed calibration features are capable of doing this independently. The photometers are equipped with an integrated calibration function that permits the measurement of

Figure 1: Photometer Spectroquant® Pharo® 100 with a choice of test kits.

bromate in the range from 0.003 to 0.120 mg/L without having to record a standard series. The analysis and sample-pretreatment processes, which require just a few chemical reagents, are described in a special application note separately prepared by Merck.

Before the bromate content can be measured, the sample must be concentrated. This enhances the sensitivity of the method, enabling it to measure concentrations right down to the µg/L range. The sample solution is then mixed with the reagents given in the application and left to react for 30 minutes, the time necessary to allow the color to develop. All working steps are described in detail in the application note and in the manuals enclosed with the Merck photometers and should be followed exactly.

The diagram below shows the comparison of ion-chromatographic and photometric measurements using samples prepared with standards with a defined bromate content. The two methods show a good agreement.

As the results show, when carried out correctly the photometric method is also well suited to permit an estimation of the bromate content. When the results lie in the region of the limit or seem doubtful for any other reasons, further-going analysis is advisable.

In addition to the standard solutions, a real sample in the form of mineral water was also tested for bromate. Mineral water typically contains a multitude of ions and due to its complexity is hence not comparable with a standard solution. The ion-chromatography method may also be fraught with problems due to the high number of other substances contained.

First the mineral-water sample was analyzed several times for bromate. These photometric measurements showed that specific constituents of the water (presumably calcium) cause a turbidity of the sample during the concentration procedure and to a certain extent also upon the addition of the reagents, resulting in false-positive measurement values. Filtration of the sample solutions yielded lower results.

The results of the photometric method were then verified by comparing them with those yielded by ion chromatogra-

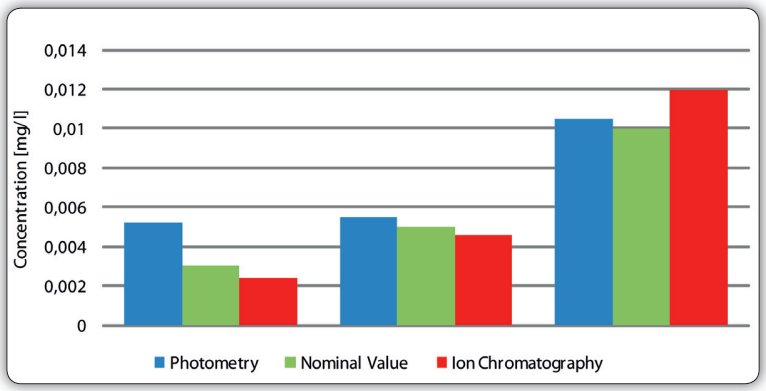

Figure 2: Comparative measurements of different bromate standards: photometry vs. conventional ion chromatography. »

phy as the established method for the determination of bromate. It must be noted here that the use of the conventional ion-chromatography method may lead to false-low results, since the strong matrix load causes interferences that lead to misinterpretations. This is why a somewhat more elaborate methodological approach is called for here.

In the ion-chromatographic method presented here, first 15 mL of mineral water was diluted with high-purity water to make a sample of 20 mL. Then the original mineral-water sample as well as a sample of mineral water spiked with 0.07 mg/L bromate were measured. The injection volume was 250 µl, using a high-capacity separation column (Dionex, type IonPac® AS9-HC) with loop injection. The eluent used was 4.5 mM sodium carbonate solution. The result was quantified by integration of the corresponding bromate peak areas. The difference between the peak areas (standard-addition method) was taken to calculate the original content, which in the case of the mineral water under investigation lay at 0.03 mg/L.

This method enables small concentrations of bromate to be reliably determined alongside the anions chloride, nitrate, and sulfate that are usually present in mineral water. The use of conventional ion chromatography may result

Sample treatment	Concentration (photometry) [mg/l]
Without filtration of turbid samples	0,063
	0,052
	Ø 0,058
With filtration* of turbid samples	0,030
	0,028
	0,028
	Ø 0,029

* Turbidity occured after evaporation and partly after addition of reagents; therefore, up to two filtration steps were conducted, using a membrane filter.

Figure 3: Bromate content, determined by photometry.

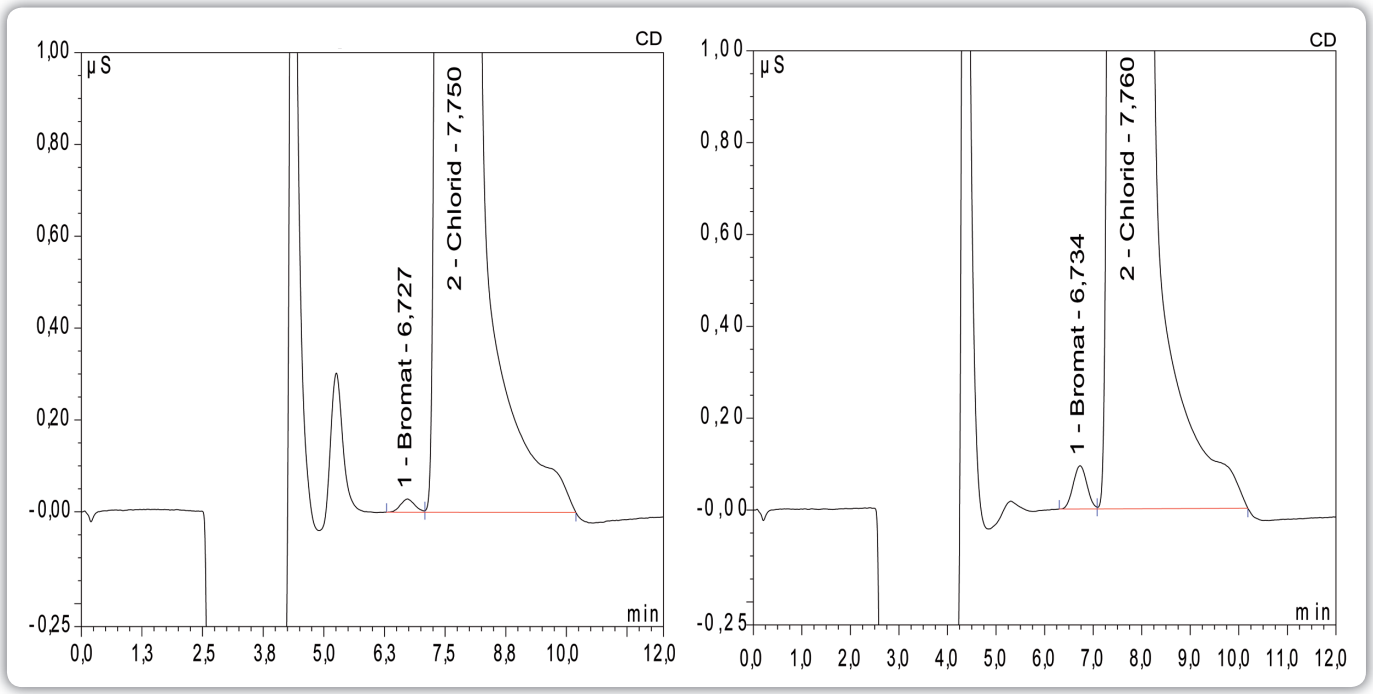

Figure 4: Details from ion chromatogramms of mineral water; left: original sample; right: mineral water spiked with 0,07 mg/l bromate.

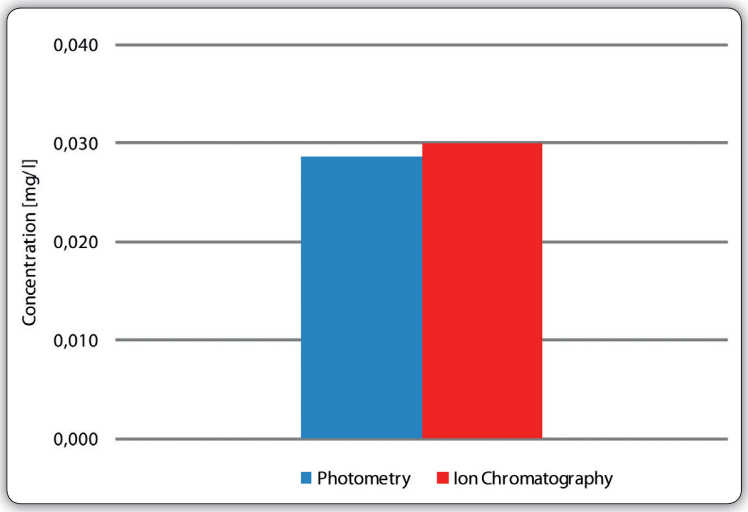

Figure 5: Comparative measurements of mineral water: photometry vs. improved ion chromatography.

in false-low findings. In our experiments this method yielded values in the region of 0.01 mg/L bromate. Here the sample was first fed through an anion-exchange column. Following this enrichment step the anions were eluted to the separation column and detected by measuring the conductivity.

Conclusion

The determination of the bromate content of water is a challenge that can be met either by using an elaborate ion-chromatography system or a photometric method. Both approaches demand careful handling and a critical appraisal of the result that is yielded. If the necessary working steps are carefully followed, photometry constitutes a true alternative to chromatography for those laboratories that do not possess ion-chromatography systems.

Methods, instruments, and chemicals

All measurements were carried out as per the application note "Bromate in Water and Drinking Water", using a Spectroquant® Pharo® 300 photometer from Merck KGaA. The calibration curve is preprogrammed on the Nova 60, Nova 60A, Pharo® 300, and Pharo® 100 photometers. The chemicals required for the measurement procedure were used as described in the application note. The individual reagents were: potassium bromate, Cat. No. 104912; potassium iodide, Cat. No. 105043; 3,3'-dimethylnaphthidine, Cat. No. 103122; acetic acid, Cat. No. 100063; and perchloric acid, Cat. No. 100519; all chemicals from Merck KGaA.

The application note for the determination of bromate is available on request at the e-mail address gunter.decker@merckgroup.com . The description of the procedure for the preparation of a bromate standard is also available at this address. The measuring range of 0.003 – 0.120 mg/L BrO_3^- is obtained in a 50-mm cell.

The modified IC measurements were carried out on the Dionex DX-300 instrument. The column used was the Dionex IonPac® AS9-HC separation column, and sodium carbonate GR, Cat. No. 103393, from Merck KGaA was taken as the eluent.

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