The analysis of potassium bromate in bakery products

Potassium bromate is recognised as one of the best dough improvers in the bakery industry. Under controlled baking conditions, potassium bromate is converted into potassium bromide, which is considered harmless to the consumer. Because scientific evidence has implicated potassium bromate as a possible carcinogen, it has been removed from the list of acceptable additives for flour treatment. The industry’s ability to reduce bromate residues to less than five parts per billion in finished bakery products will determine if potassium bromate will be included again in future lists. Consequently a fast, reliable and easy means of detecting low levels of bromate residues is required.

by Ade Kujore and Josep-Miquel Serret
Potassium bromate (KBrO₃) is produced industrially as white crystals, which are soluble in water. The compound is a very strong but slow-acting oxidiser.

Potassium bromate has excellent flour improvement (E 924) qualities and has been/is used in the industrial production of bakery goods, mainly having its action during the later dough-making and early baking stages.

During the proofing stage of bread-making, high levels of protein (glutens) in the flour trap gas bubbles and cause the dough to ‘rise’. Potassium bromate facilitates this process in flours with lower levels of glutens so that they perform in the same manner, resulting in bread which is strong, voluminous and elastic, and which contains small evenly-sized gas bubbles. The resulting bread appears springy. Potassium bromate also bleaches white flour slightly, helping to produce a creamy white colour.

In the heat of the baking oven, potassium bromate is reduced to potassium bromide, which is considered to be innocuous in the finished baked product.

2KBrO₃ ----> 2KBr + 3O₂

It is assumed that all the added bromate is reduced to bromide. However, this is dependent on the oven temperature, the duration of exposure at that temperature, the amount of azodicarbonamide present and the quantities of potassium bromate used. It is therefore conceivable that some bromate residue may be left in the finished baked product.

In the United States, potassium bromate has been used by the baking industry for almost a century without its use raising any health issues. However, with the advent of the use of ozone for the industrial disinfection of water, it was noted that a complex reaction took place, involving increases in the temperature of ozonation, bromide ion concentration, hydrogen peroxide content and pH. The overall result was an increase in bromate concentration in the water.

Since bromate is now considered to be a potential carcinogen in humans, and is also thought to induce impairment of renal and aural functions, such increased concentrations of bromate in water gave rise to worries about eventual residual potassium bromate in bakery products. Although no harmful effects resulting from potassium bromate in bakery products have ever been explicitly proven, such concerns have led to an evaluation of its use in baking.

In the United States, because the FDA had previously sanctioned the use of potassium bromate in bakery products, it was deemed under the so-called ‘grandfather clause’ to be unconstitutional to subsequently ban its usage. Consequently, in the United States, a maximum residual concentration of 20 parts per billion (ppb) is permissible within the finished bakery products. As a precautionary measure, many other countries have banned any use of potassium bromate in bakery products. However, there are calls to re-examine this latter position, dependent upon the industry’s ability to reduce bromate residual levels to less than 5 ppb in finished bakery products. In the meantime, various other chemicals are now being used as flour improvers; these include azodicarbonamide, potassium iodate and ascorbic acid/phosphate, glucose oxidase, pentosanase or xylanase, phospholipase, xylanase, alpha amylase, fava bean and soy bean flour.

In order to check compliance with food regulations and perhaps drive future legislation, food processing chemists and regulatory bodies require a fast, reliable, sensitive, accurate, specific and easy method of determining bromate levels in finished baked goods. Whichever method is used, the complex matrix in samples of bakery products dictates that a degree of sample pre-treatment is required.

**Methods of detecting residual bromate levels**

There are several existing methods for the determination of bromate, all with their advantages and disadvantages:

- A spectrophotometric method, based on the reaction of bromate with 3,5-dibromo-PADAP and thiocyanate in an acidic medium, is relatively simple but has a limit of detection of around 18 ppb. Because a lower limit is required in finished bakery products, this method is therefore not always suitable. The method also requires extensive sample pre-treatment.

- Flow through fluorescence methods, based on derivatisation reactions, have a limits of detection of around 1 ppb but are not are simple. These methods also involve the use of quite extensive sample pre-treatments.

- IC/Mass spectrometry provides detection limits of around 5 parts per trillion (ppt) so is easily sensitive enough, but the instrumentation required is relatively complex and expensive.

- Ion Chromatography (IC), involving the use of suppressed conductivity detection is useful, as a relatively small amount of sample pre-treatment is required. However suitable low limits of detection are not always possible and the matrix effect of chloride is pronounced.
The use of suppressed conductivity IC coupled to post column derivatisation High Performance Liquid Chromatography, does provide limits of detection down to around 0.1 ppb, but the analysis can be complex and expensive.

An HPLC method for analysis of bromate
Straightforward High Performance Liquid Chromatography (HPLC), involving post column UV/Visible detection has proved to be very successful at detecting bromate levels of 0.2 ppb, without extensive sample pre-treatment. The method outlined here uses o-dianisidine (ODA) as a post column derivatising reagent. Other post column reagents, such as potassium iodide or fuchsin may be used instead with the same HPLC equipment.

HPLC is a well-established technique for the determination of many analytes. It can be easy to operate, fast, accurate, reproducible, reliable, specific and sensitive. The technique frequently allows all the members of a group of analytes to be determined within the same chromatographic run, with little or no sample pre-treatment being required.

For the analysis of bromate, the required criteria for a commercial modular HPLC system with UV/Visible detection are accuracy, speed, reproducibility, reliability, specificity and sensitivity. The detector must allow for low noise, have high sensitivity and low drift, be tolerant to fluctuations in the temperature of the eluent and have a wide dynamic range and fast response times. The HPLC system also needs to be easy to operate, with effortless post column derivatisation facilities and column heater/chiller options.

Here we highlight the ability of a Cecil Instruments Adept HPLC system 2, for use in the determination of bromate in samples of bakery products. This particular commercial system includes a UV/Visible detector, an isocratic pump, an online post column derivatisation reactor, a column heater and chromatography control, as well as acquisition and processing software.

Standards and bromate-spiked samples of white bread were injected onto an Adept HPLC system 2, under the conditions shown in Table 2.

The chromatogram in Figure 3 shows a clearly resolved peak for bromate in a bread sample spiked with bromate at 1 ppb, thus showing the suitability of the system for the determination of low ppb levels of bromate in bread. In addition, there is no need for protracted sample preparation steps or complex chromatography systems. The technique may be automated, and may also be used for other sample types, such as raw ingredient potassium bromate and other finished baked goods.

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Table 2. Experimental conditions used for HPLC analysis of bromate.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column:</td>
<td>Novosep A-2 Anion, 5 µm 250 x 4 mm.</td>
</tr>
<tr>
<td>Mobile Phase:</td>
<td>3.6 mM Sodium Carbonate.</td>
</tr>
<tr>
<td>Flow Rate:</td>
<td>0.85 mL/min.</td>
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<tr>
<td>Detector:</td>
<td>UV/Visible at 450 nm.</td>
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<tr>
<td>Column Temperature:</td>
<td>40 °C</td>
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<tr>
<td>Injection Volume:</td>
<td>200 µL pre-treated sample (pre-treatment was homogenisation in water, then centrifugation) or standard.</td>
</tr>
<tr>
<td>Post Column Reagent:</td>
<td>Potassium bromide in dilute nitric acid/methanolic o-dianisidine dihydrochloride solution.</td>
</tr>
<tr>
<td>Post Column Reaction:</td>
<td>150 µL reactor volume, 60 °C. Flow rate of 0.7 mL/min.</td>
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<tr>
<td>Run Time:</td>
<td>20 minutes.</td>
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</table>

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