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Note

Determination of iodide in dairy products and table salt by ion chromatography with electrochemical detection

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The use of iodine-containing feed supplements and teat dips in the farming industry has resulted in significant increases in the concentration of iodide in milk. Because of its toxicity, excessive intake of iodine is cause for health concern [1]. Since from 25% to more than 50% of the dietary intake [1,2] of iodine is from milk and dairy products in the form of iodide, a simple and reliable method for the routine determination of iodide in such products is desirable.

Several methods are available for the determination of iodide in milk. Microchemical methods require acid digestion [2] or alkaline ashing [3] of the sample prior to quantification based on the modified Sandell–Kolthoff reaction. A gas chromatographic method with electron-capture detection involves making an iodobutanone [4] or 2-iodoethanol [5] derivative. A differential-pulse polarographic method [6] also requires ashing. Iodide has been determined by ion chromatography with UV detection following combustion of the sample in a Schöninger flask [7]. Except for the gas chromatographic method, which determines inorganic iodine, the above methods give the total iodine content of milk.

As most of the iodide in milk is in the ionic form [8], iodide-specific electrodes [1,9] can be used and are the simplest of all the detection devices. However, the electrode response is slow at low iodide concentrations and the approach is subject to interference from free sulphydryl groups in pasteurized milk and dairy products [1].

In the method proposed here, precipitation of milk proteins and most of the fat is effected by addition of methanol. The remaining organics are removed by means of a C_{18} solid-phase extraction cartridge before ion chromatographic separation and electrochemical detection of iodide. Table salt is simply diluted, filtered and directly analysed by high-performance liquid chromatography (HPLC).

EXPERIMENTAL

Reagents

Degassed Milli-Q water (Millipore, Bedford, MA, U.S.A.) was used for making solutions. The mobile phase consisted of 0.0055 *M* KH_2PO_4 at its natural pH of about

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5. For solid-phase extraction clean-up, Waters Assoc. Sep-Pak C_{18} cartridges and 0.45-μm filters were used. A 500 μg/ml iodide stock solution was prepared from potassium iodide and dilutions were made as necessary. Milk and other samples were purchased from local supermarkets. Spiking of milk was done by diluting 0.2 ml of appropriate concentrated aqueous iodide standard to 100 ml with milk.

Liquid chromatography

The HPLC system consisted of a Beckman Model 112 solvent-delivery module, a Model 420 controller and a Model 340 organizer with a 50-μl loop. A Bioanalytical Systems LC-4B amperometric detector was used with a silver working electrode at 0.155 V and 0.005 in. film thickness. Peak areas were computed with a Spectra Physics SP 4270 integrator. A Vydac 302 IC (Separations Group, Hesperia, CA, U.S.A.), column (250 × 4.6 mm I.D) preceded by a Vydac ion guard column was used for separations. The mobile phase flow-rate was maintained at 2 ml/min.

Sample preparation

Milk. A 25-ml volume of milk was incubated in a 150-ml beaker in a water-bath for 3 min at 38°C. Following this, 50 ml of analytical-reagent grade methanol were added, the solution was mixed by swirling and the beaker was left in the bath for a further 3 min. The sample was allowed to stand at room temperature for 30 min and then filtered through Whatman No. 1 filter-paper. After another a further 30 min about 4 ml of clear filtrate were passed through a Sep-Pak C_{18} cartridge. The first 2 ml of the eluate were discarded and the remainder was filtered through a 0.45-μm filter for analysis.

Other samples. Yogurt and cream were treated in the same way as milk. For instant milk powder an 8–10% solution in water was prepared and then treated as for milk. For processed cheese, a 10-g sample of cut pieces of cheese was weighed in a 150 ml beaker and mixed with water to give about 50 ml of sample. The sample was homogenized (Polytron) for 1 min and the homogenate was diluted to 100 ml with methanol, homogenized again and filtered. A 4-ml volume of the filtrate was passed through a Sep-Pak C_{18} cartridge and the remainder of the procedure for milk was followed.

Procedure

A 100-μl aliquot of the sample filtrate was injected into the HPLC system. Iodide was determined by comparing the peak areas of the sample and the standard treated in exactly the same manner.

RESULTS AND DISCUSSION

Three different ion chromatographic columns were evaluated for the separation of iodide in milk sample extracts. Fig. 1 shows typical chromatograms obtained. Although all three columns performed well for pure iodide standards, there were signifiant differences when actual samples were analysed. With the Partisil 10 SAX column (Whatman) (A), the iodide peak was immediately preceded by another peak of almost equal height. In the case of the IC Pak Anion column (Waters Assoc.) (B). a huge matrix peak followed the iodide peak, thus affecting quantification. The best

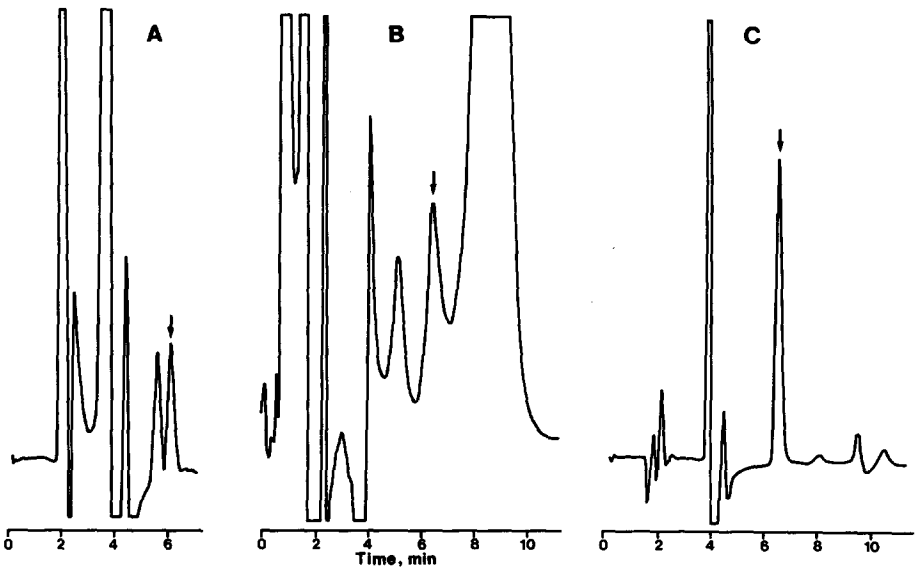

Fig. 1. Chromatograms of a whole-milk extract obtained under different conditions. (A) Partisil 10 SAX; mobile phase, 0.0065 *M* KH_2PO_4 (pH 6.2) at 2 ml/min. (B) IC Pak Anion; mobile phase, 0.005 *M* *p*-hydroxybenzoic acid (pH 10.5) at 0.9 ml/min. (C) Vydac 302 IC; mobile phase, 0.0065 *M* KH_2PO_4 (pH 6.3) at 2 ml/min.

TABLE I

IODIDE IN DAIRY PRODUCTS

Sample	Iodide (μg/l)
Milk:	
Brand A:	
Whole	363
2% fat	633
Skim	529
Brand B:	
Whole	730
2% fat	1074
Skim	480
Brand C:	
Whole	244
2% fat	236
Skim	273
Chocolate milk	350
Yoghurt	351
Half-and-half cream	350
Instant milk powder[a]	3000 μg/kg
Processed cheese (brick)	320 μg/kg

[a] Normally diluted *ca.* 10-fold before consumption.

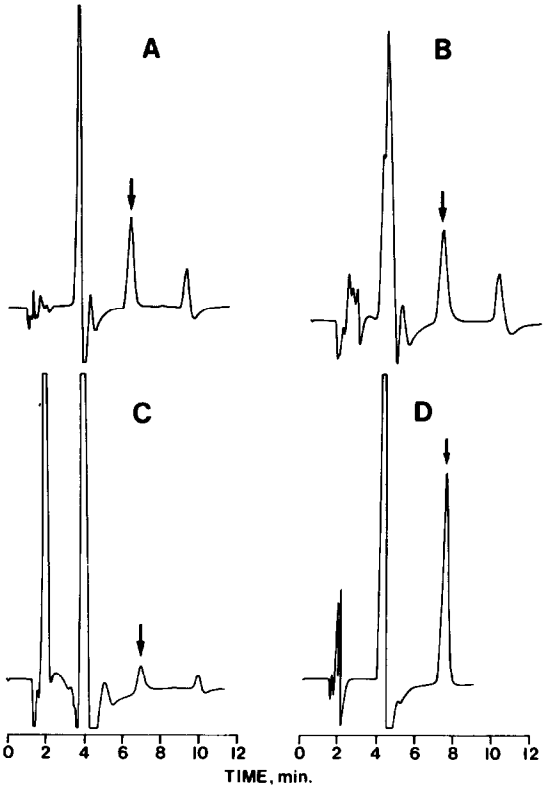

Fig. 2. Typical chromatograms obtained using the procedure described in the text. (A) Instant milk powder; (B) yogurt; (C) processed cheese; (D) table salt.

results were obtained with a Vydac 302 IC column (Separations Group) (C), where the iodide peak was clearly separated from the other sample components.

Several ionic reagents were checked for precipitation of proteins in milk. Some of them were found to be electroactive under the chromatographic conditions chosen and either gave a large response close to iodide elution time or resulted in a high background. Precipitation of proteins by adding an equal volume of acetonitrile [7] to milk was found to be satisfactory. However, it was observed that the response of iodide increased with repeated injections of filtrate. This effect was substantially reduced when methanol was used as the precipitant. No significant change in peak area was noticed on repeated injections over a 1-h period.

The detector response to iodide was linear in the range 2–100 ng injected. Replicate determinations on 25-ml aliquots of a whole milk sample gave a relative standard deviation of 3.3% at a level of 600 μg/l. The recovery of iodide at levels of 400 and 800 μg/l added to milk was 99% and 114%, respectively. Yogurt, chocolate milk, half-and-half cream, instant milk powder and processed cheese gave recoveries of 92, 100, 110, 99 and 103%, respectively. The detection limits were about 25 μg/l for the foods examined.

Table I presents results obtained for a variety of dairy products. The values for

milk ranged from 236 to 1074 μg/l iodide with an overall average of 507 μg/l, which compares well with earlier data for milk from this geographical area [2] obtained using a completely different technique. The wide range of values is probably due to the difference in the use of iodophors within the dairy industry. The concentration of iodide was not related to the fat content of the milk. The other dairy products analysed had iodide concentrations within the range found for the milk products (instant milk powder being diluted *ca.* 10-fold before consumption). Fig. 2 shows some typical chromatograms obtained using the described method. No interferences or technical problems were encountered with any of the sample types examined.

Confirmation of the iodide peak in selected samples was carried out by adding silver nitrate to the sample extract to precipitate the iodide. The extract was then passed through a cation-exchange solid-phase extraction tube (Supelco) to remove the silver ions and then an aliquot was injected into the HPLC system. The iodide peak was completely removed by the silver nitrate treatment indicating that it was, indeed, iodide (bromide, chloride and fluoride elute with different retention times).

Iodide in table salt was determined using the same HPLC system. Table salt was simply dissolved in water (0.2%, w/v), filtered and analysed for iodide. No interferences from chloride were observed (see Fig. 2). The recovery of iodide from table salt was 94% at a 100 μg/g spiking level. A similar technique using electrochemical detection with a platinum electrode and different chromatographic conditions has been reported recently [10].

The method described is simple, sensitive and selective. It may be adapted to the determination of ionic iodide in other food types.

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