Proof of Authenticity of Pure Instant Coffee*

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Abstract

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An HPLC method with refractometric detection was worked out for the determination of the limiting contents of marker saccharides (free mannitol and total glucose and xylose) used for the proof of authenticity of pure instant coffee. This method, even though more laborious, yields results comparable with those obtained by the HPAE-PAD method and is intended mainly for those laboratories where the current HPLC technique with refractometric detection is presently used for saccharide analysis. The survey of market supply showed that instant coffee imported in bulk and subsequently packaged in the Czech Republic is most frequently adulterated – only one out of 7 samples examined contained authentic coffee. On the other hand, only one out of 10 samples of instant coffee imported in original packaging did not meet the authenticity criteria. The samples of instant coffee by domestic producers indicated that one producer placed on the market an adulterated product, whereas the other brand is authentic coffee.

Key words: instant coffee; authenticity; adulteration; HPLC with RI detection

After the switchover of the Czech Republic to the market economy system, connected with the effort to enter international trade structures, especially the European Union, prominence has been given to the issue of food adulteration. In the former Czechoslovakia only a negligible attention was paid to this problem because no economic necessity or public opinion pressure existed that would require any solution. On the other hand, the western countries have been pursuing the monitoring of food adulteration for a long time. It is of importance in international trade, both between the EU countries and worldwide, particularly where developing countries are involved. Strong interests of national and supranational consumer associations in the protection of their member interests also are felt here. In this connection, it should be stressed than foreign countries very frequently use the term "food authenticity" instead of "food adulteration", also meaning the conformity of a product with its prescribed and declared quality properties, including their origin.

One of the products which is monitored abroad for authenticity is pure instant coffee. It is obtained by water extraction of ground roasted coffee beans at 100–180°C, yielding 35–55% of soluble substances. The cooled extract is then either dried in spray drier or lyophilised, in both cases to 1–5% of moisture content.

ICO (International Coffee Organisation) defines soluble coffee as "the dried water-soluble solids derived from roasted coffee" (ICO 1982). ISO (International Organization for Standardization) uses the terms instant coffee, soluble coffee or dried coffee extract and defines them as "dried, water soluble product, obtained exclusively from roasted coffee by physical methods using water as the only carrying agent which is not derived from coffee" (ISO 3509). Within the European Union, the terms soluble coffee, instant coffee, dried coffee extract or dried extract of coffee all mean "coffee extract in powder, granular, flake, cube or other solid form, of which the coffee-based dry matter content is not less than 95% by weight"(Directive 1999/4/EC). It is also stipulated that "this product shall not contain any other substances than those derived from its extraction". The Czech procedural regulation No. 330 of Food Act No. 110/1997 Sb. took over practically the definitions of the EU (Vyhláška č. 330/1997 Sb.). In other words, a commodity labelled as pure instant coffee, or bearing other labels accepted by ICO, ISO and EU, may not contain any other substances than those derived from roasted coffee beans.

In spite of all the legislation protecting the authenticity of instant coffee, attempts to adulterate it appeared very soon. This has been practised by the addition of various plant materials that only negligibly influence sensory properties of the final product, but bring an unjustified profit to the adulterer due to the markedly lower price of the substance added. It was also shown that instant coffee was

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most frequently adulterated by the addition of coffee husks and parchments, then by maltodextrins and caramelised sugar, cereals, malt, chicory and dried figs (PRODOLLIET 1995). It is only natural that the world's recognised producers of instant coffee answered this situation by a search for an analytical method that would provide an unequivocal proof of coffee adulteration. Such a method was then based on the determination of the pattern of saccharides characteristic for authentic instant coffee.

BLANC *et al.* (1989) were the first to prove instant coffee adulteration who used as markers monosaccharide contents determined by the HPLC method, with postcolumn derivatisation by a solution of tetrazolium blue and spectrophotometric detection. They determined the content of both "free monosaccharides" and so-called "total monosaccharides", i. e., saccharide content found after 4-hr coffee hydrolysis by boiling with 0.1N H_2SO_4 under a reflux condenser. A similar method, complemented by mannitol determination, was used for the same purpose by DAVIS *et al.* 1990). The possibility of enzymatic determination of saccharides was also examined (BERGER 1991). However, this method was not recommended, being only applicable to small amounts of added adulterants. On the basis of an extensive study, Prodolliet et al. (PRODOLLIET *et al.* 1991, 1995a, b) recommended the HPLC method with pulsed amperometric detection (HPAE-PAD) for the determination of marker saccharides. It is fast, accurate and sufficiently sensitive. This method was also collaboratively tested (PRODOLLIET 1995c, 1996) and published as an international standard ISO 11292.

After the evaluation of all data available, it was possible to compile saccharide profiles of both authentic and adulterated instant coffee (PRODOLLIET, HISCHENHUBER 1997). Pure coffee is characterised by low content of free monosaccharides and a high content of total galactose and total mannose. Coffee adulterated by the admixture of coffee husks or parchments contains high levels of free mannitol and fructose and total glucose and xylose. Adulteration by the addition of cereals, malt, maltodextrins and caramelised sugar increases the amount of free glucose, fructose or also saccharose and simultaneously the level of total glucose is raised substantially. The adulteration by chicory results in the increase of free and total fructose. Along with this, the limit contents of marker monosaccharides in dry matter of authentic instant coffee were determined (in %/d.s.) (PRODOLLIET 1995; WOOLFE 1997):

Indicator carbohydrates	maximum limit	Experimental variability interval	control limit
Free mannitol	0.3	0.2	0.5
Free fructose	0.6	0.4	1.0
Total glucose	2.1	0.5	2.6
Total xylose	0.4	0.2	0.6

These limits have been recently taken into account for the compilation of the Code of Practice for the Soluble Coffee Industry in the UK (CODE ... 1995).

It was possible to reasonably suppose that adulterated coffee could be sold in the Czech Republic similarly like in the other European countries. It therefore became relevant to monitor also its authenticity in the domestic retail network. Our intention was to verify the possibility of using the HPLC method with refractometric detection for such an inspection. This combination, which is currently used in our laboratories dealing with saccharide analysis, has never before been published in this connection. It was also decided to carry out a preliminary survey of the domestic retail network to evaluate the incidence of instant coffee adulteration.

MATERIAL AND METHODS

Demineralised water max 18 MΩ/cm and chemical reagents, including saccharide standards, of analytical grade were used in all experimental work.

Sample pretreatment cartridges: Silica-cart C_{18} (Tessec Co.); Hema-cart DEAE (Tessec Co.); Hema-cart SB (Tessec Co.); On Guard-Ag (Dionex Co.); Membrane filter 0.45 μm (Tessec Co.); Chromatographic column 8 × 250 mm, packed with OSTION LGKS 0800 in Pb^{++} form (Watrex Co.); Liquid chromatograph Spectra Physics P200; Differential refractometer Chrom 4-7490 (Merck Co.); Chromatographic station CSW (fa Data Apex Ltd.)

The samples of instant coffee to be evaluated were purchased from food retail outlets.

Dry matter was determined from weight loss after drying a precisely weighed sample at 105°C for 3 hrs, expressed in %.

Determination of Free Mannitol: The amount of 1.25 g of tested sample was transferred into a 25ml volumetric flask. Some 15 ml of demineralised water was added and the flask was shaken at ambient temperature until the sample was dissolved. Water was then added to 25 ml, the content mixed and its part poured into a centrifugal cell and centrifuged for 10 min at 10 000 to 14 000 rpm. The clear brown supernatant was decanted. Exactly 0.75 ml of it was precisely pipetted and passed through a set of cartridges C_{18}, SB and DEAE under reduced pressure. These cartridges were pre-conditioned and washed with demineralised water. The eluate from the cartridges and water from at least three subsequent washings was collected into a 10ml volumetric flask. Water was added to 10 ml, the content was mixed and finally filtered through a membrane filter, yielding a sample ready for injection into the chromatographic column.

Determination of Total Glucose and Xylose: The amount of 1.25 g of tested sample was transferred into a 25ml volumetric flask, mixed with 12.5 ml of 1M HCl and kept in boiling water bath for 150 min with periodic stirring (approx. each 30 min). After cooling water was added to the hydrolysate to 25 ml, the content was mixed and a part of it was poured into a centrifugal cell and centrifuged for 10 min at 10 000 to 14 000 rpm. The clear brown supernatant was decanted. Exactly 0.75 ml of it was precisely pipetted and passed through a set of cartridges On Guard-Ag, C_{18}, SB and DEAE under reduced pressure. These cartridges were pre-conditioned and washed with demineralised water. The eluate from the cartridges and water from at least three subsequent washings was collected into a 10ml volumetric flask. The content was filled up with water to 10 ml, mixed and finally filtered through a membrane filter, yielding a sample ready for injection into the chromatographic column.

Chromatography conditions: injection 20 µl, column temperature 75°C, mobile phase – demineralised water and flow rate 0.3 ml/min.

Relative standard deviation (replicate determination; $n = 7$): total glucose 2.0%, total xylose 7.4% and free mannitol 7.5%.

Recovery (standard additions of saccharides to 100 g coffee sample: mannitol 1.2 mg; xylose 2.4 mg; glucose 12.6 mg): total glucose 101.5%, total xylose 95.6% and free mannitol 108.6%.

Detection limit for all carbohydrates was 0.05%.

RESULTS AND DISCUSSION

The implementation of the analytical method for the proof of instant coffee authenticity, based on the determination of marker saccharides by HPLC with refractometric reaction, showed at an early stage that this modification is feasible, in principle. A chromatographic column packed with OSTION LGKS 0800 in Pb^{++} form was used. It enabled the separation with sufficient resolving ability of the whole spectrum of standards of those saccharides that could occur in instant coffee (Fig. 1). The sensitivity of the refractometric detection of the standards of marker saccharides was also acceptable for the determination of their limiting contents.

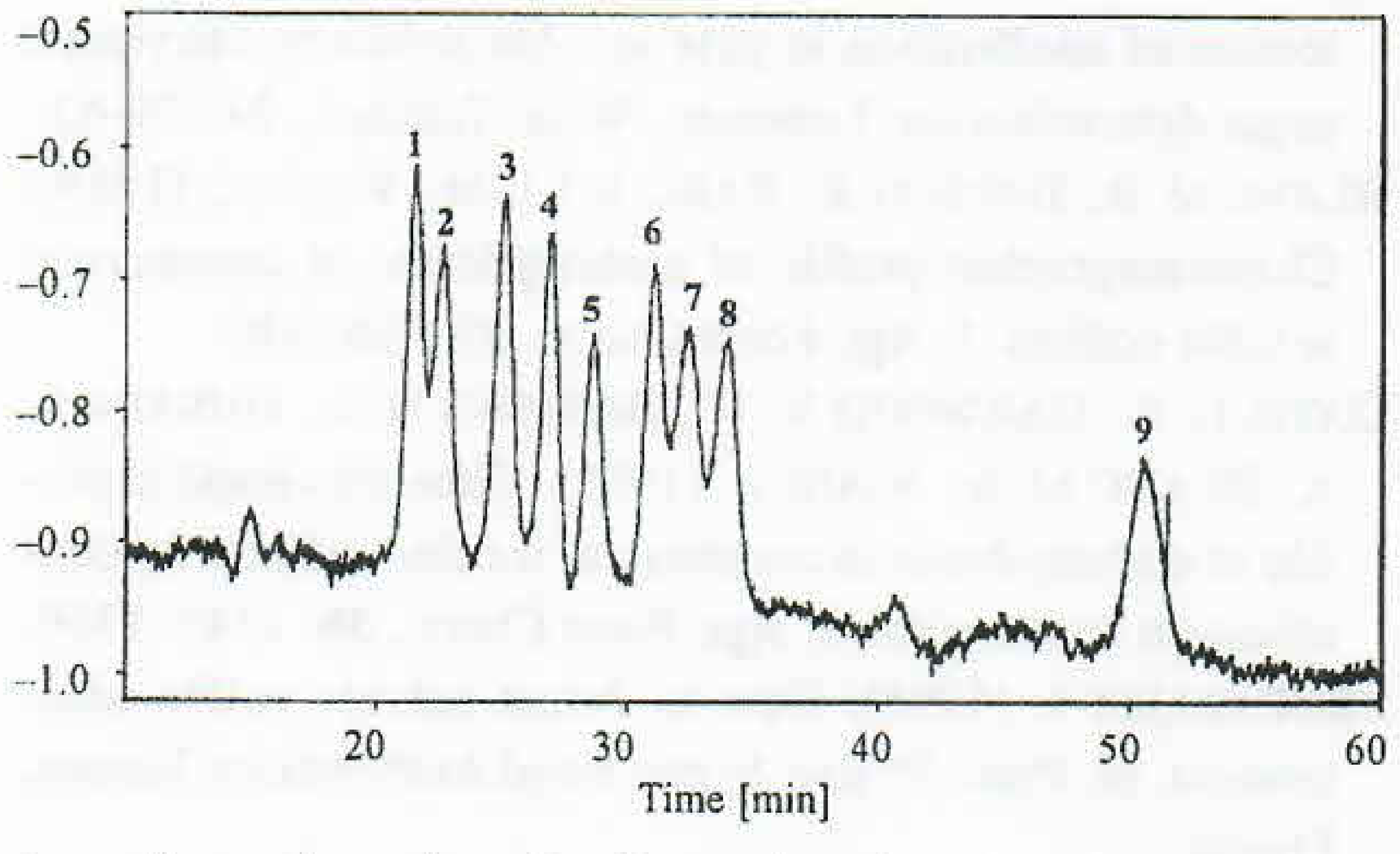
The basic problem therefore consisted in the design of a highly efficient system of sample purification, which has the basic importance for the refractometric detection if compared with other detection systems (e.g., PAD). The removal of impurities is here unavoidable to eliminate possible co-elution of ballast substances that show identical refractive index as marker saccharides, i.e., it preconditions the success of the whole chromatographic process. The presence of impurities also has an unfavourable influence on the background line, thus reducing the sensitivity of the determination of small amounts of saccharides.

The purifying procedure used by us can be divided into two main steps:

- at the first instance, suspended solid impurities are removed from the samples of dissolved instant coffee by 10 min centrifugation at 10 000 to 14 000 rpm;
- dissolved ballast substances of both organic and inorganic nature are then removed from the supernatant by purification through a system of cartridges.

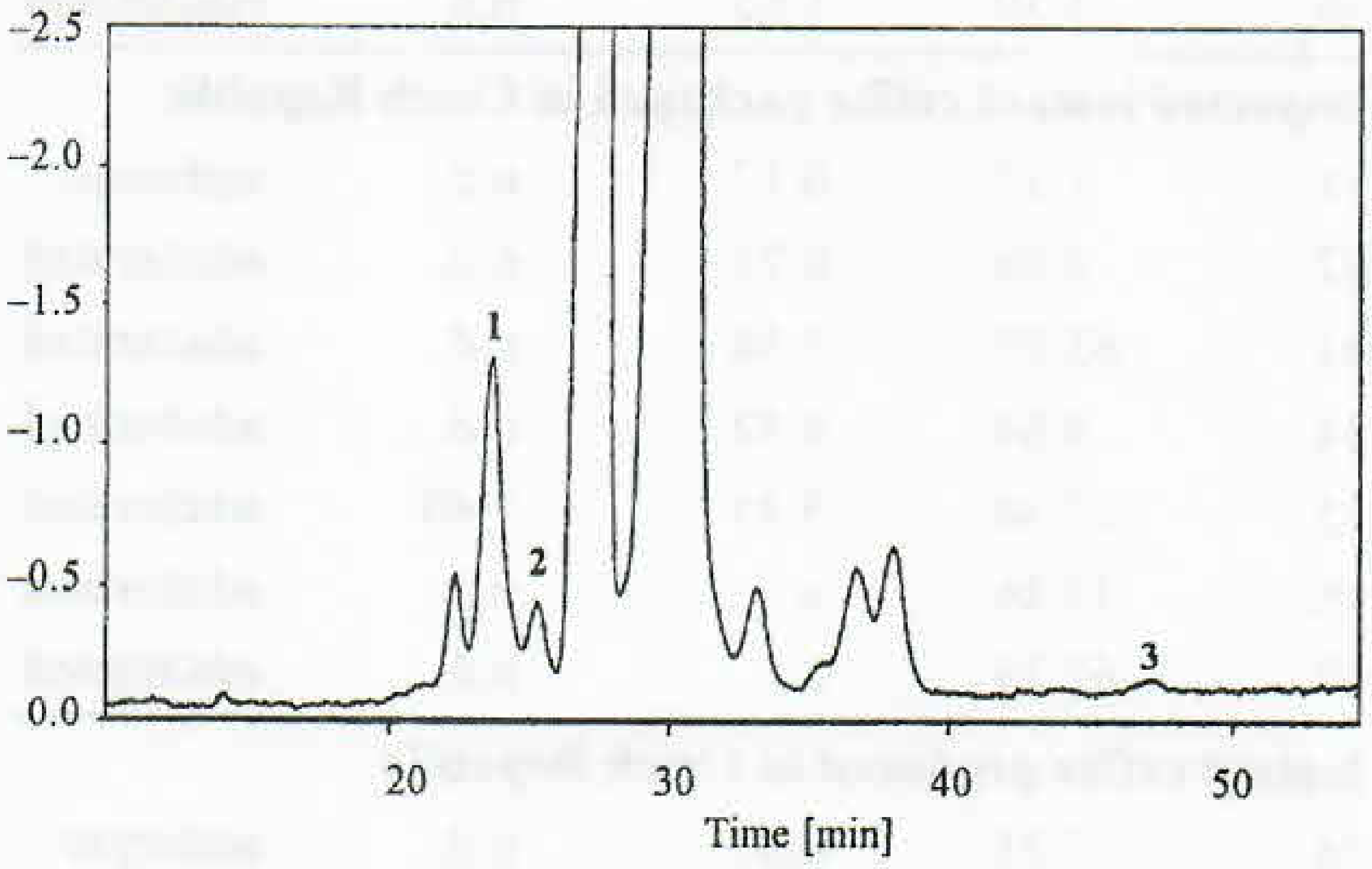
In coffee solution without hydrolysis, the cartridges Silica Cart C_{18}, Hema cart DEAE and Hema cart SB were used. The cartridge C_{18} removed hydrophobic compounds (some of them cause strong brown colouring of the extract) and the cartridges SB (highly acid cation exchanger) and DEAE (slightly basic anion exchanger) removed ionic compounds from the extract. In a coffee solution previously hydrolysed with diluted hydrochloric acid it is necessary to remove the Cl^- ions as much as possible, otherwise they would destroy the column in Pb form after injection. The cartridge On-Guard-Ag (Dionex Co.) was therefore inserted before the above-mentioned cartridges. It contains a silver form of a high-capacity, highly acid ion exchanger, which further removes a number of ions, primarily Cl^-.

The content of free mannitol and total glucose or xylose was determined both in authentic instant coffee (Fig. 2) and in instant coffee adulterated by the addition of various substances (Fig. 3 and 4) by the procedure fully described above. The content of free fructose was not observed because the recognition of fructose as a marker and the determination of its control limit was at a negotiation stage at the time of our survey. It can therefore be stated that the method of the determination of marker saccharides in instant coffee worked out by us, utilising HPLC with refractometric detection, yields satisfactory results, even though it is more laborious than the more modern



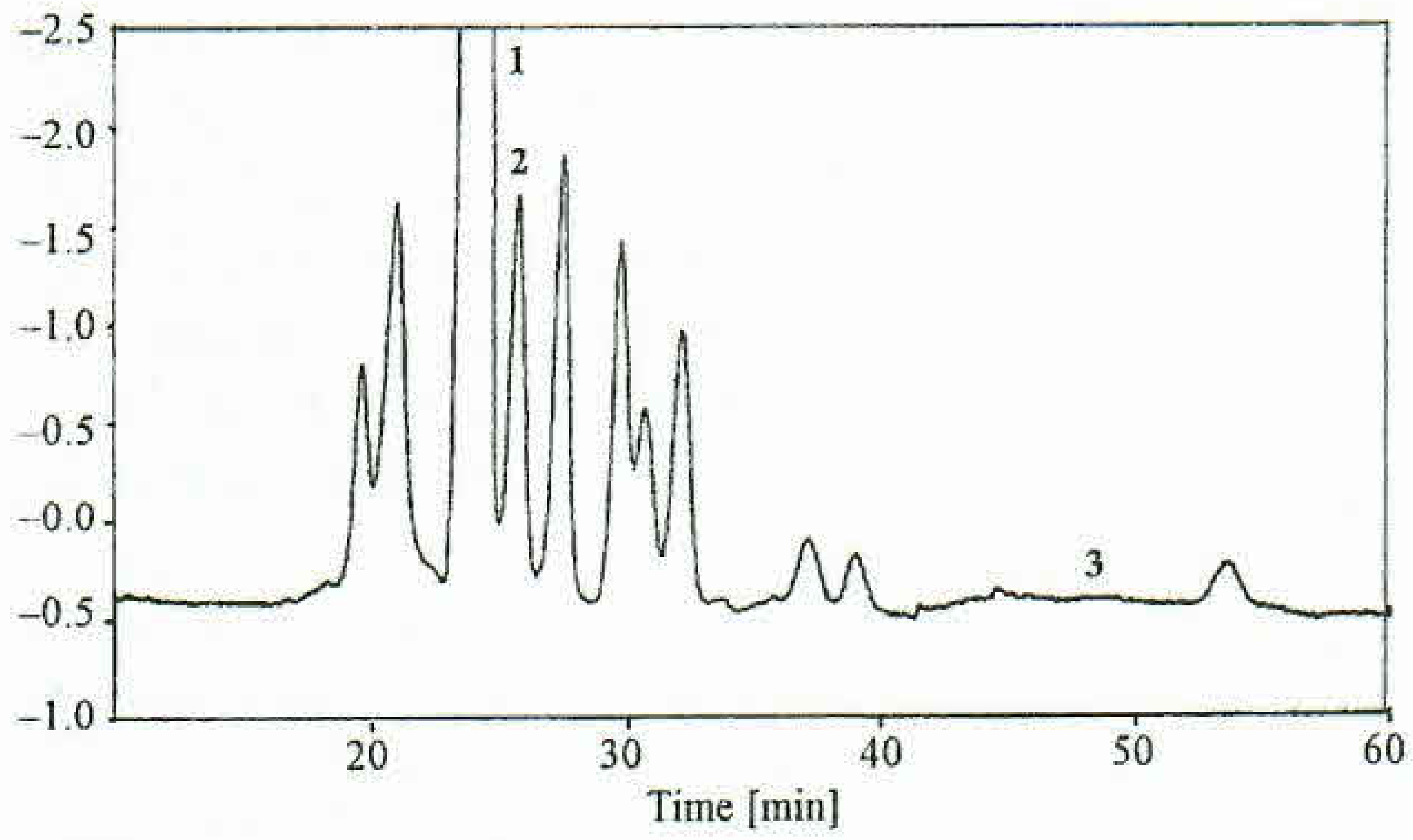
1 – saccharose; 2 – maltose; 3 – glucose; 4 – xylose; 5 – galactose; 6 – arabinose; 7 – mannose; 8 – fructose; 9 – mannitol

Fig. 1. Chromatogram of saccharide standards mixture separated on column OSTION LGKS 0800 in Pb^{++} form



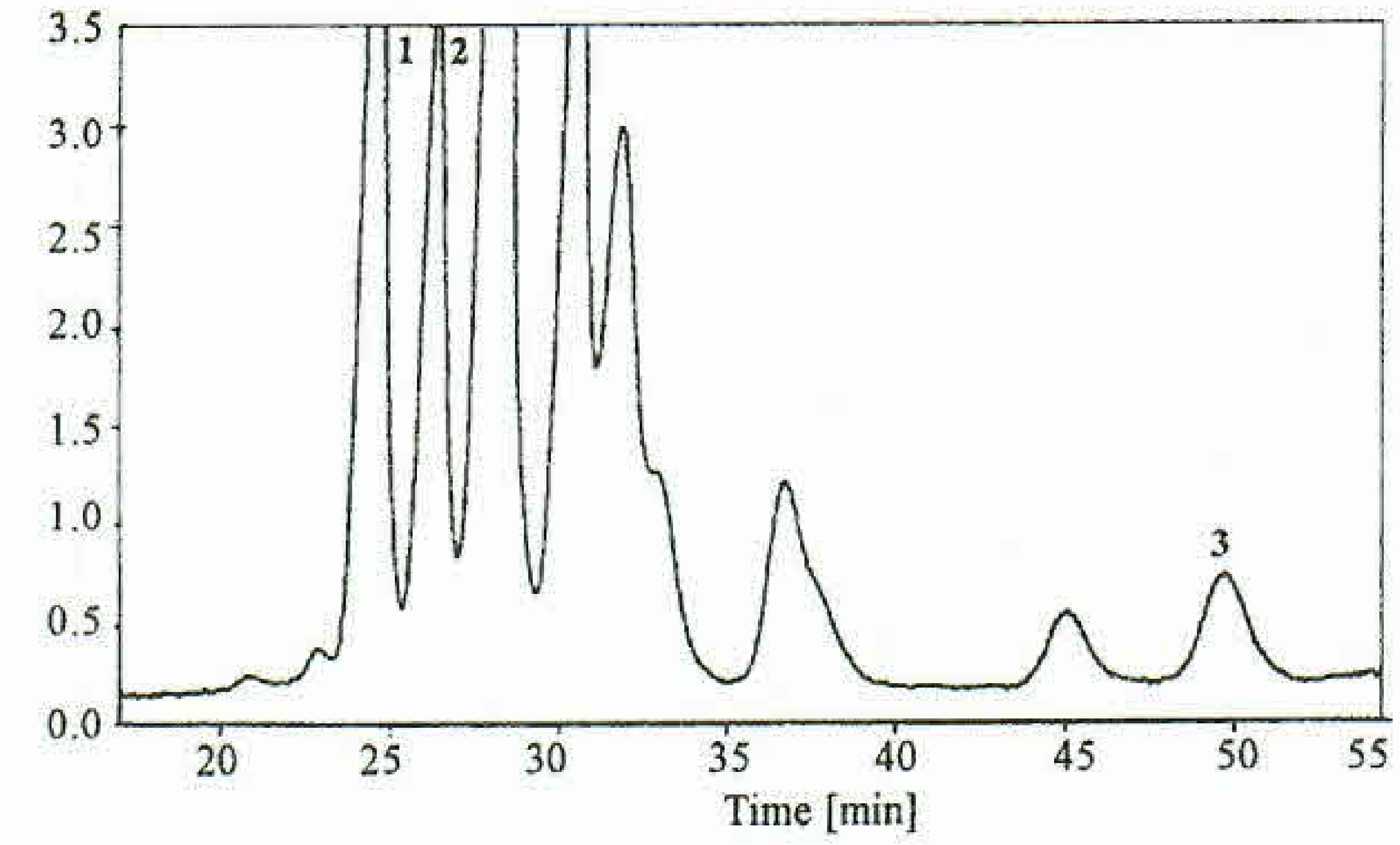
1 – glucose; 2 – xylose; 3 – mannitol

Fig. 2. Chromatogram of authentic instant coffee



1 – glucose; 2 – xylose; 3 – mannitol

Fig. 3. Chromatogram of instant coffee adulterated with addition of cereals, malt or maltodextrins



1 – glucose; 2 – xylose; 3 – mannitol

Fig. 4. Chromatogram of instant coffee adulterated with addition of coffee husks and parchments

HPAE-PAD method. It is primarily intended for laboratories provided only with conventional equipment for saccharide analysis.

As for the survey of the domestic market for the incidence of instant coffee adulteration, 19 samples were examined. Out of these, 10 were imported in original consumer packaging, 7 were domestic packaging of bulk-imported coffee, and 2 samples were products manufactured in the Czech Republic. The results of content determination of marker saccharides listed in Table I show that:

- with one exception, the samples originating from recognised foreign producers and sold in original retail packs can be classified as authentic;
- in instant coffee manufactured locally the authenticity criteria were only met by one sample, whereas the other sample slightly exceeded the content limits of all marker saccharides;
- the most unfavourable situation was found in instant coffee imported in bulk and subsequently packaged in the Czech Republic, where only one out of 7 samples examined met the criteria of authenticity.

This survey makes it possible to conclude that the threat of adulteration is most severe in imported coffee packaged locally, where the Czech organizations obviously do not check the authenticity of their imports consistently and only rely upon the parameters declared by the suppliers.

Table 1. Content of marker saccharides in samples of instant coffee from retail network

Sample No.	Saccharide content [% dry matter] after hydrolysis glucose	xylose	free mannitol	classifiation
Imported instant coffee in original packaging				
1	1.01	0.19	n.d.	authentic
2	0.93	0.15	n.d.	authentic
3	2.25	0.38	0.11	authentic
4	0.93	0.14	n.d.	authentic
5	0.48	0.19	n.d.	authentic
6	1.89	0.42	0.06	authentic
7	0.99	0.22	n.d.	authentic
8	1.24	0.26	n.d.	authentic
9	2.64	0.40	0.05	authentic
10	4.30	1.63	n.d.	adulterated
Imported instant coffee packaged in Czech Republic				
11	1.17	0.17	n.d.	authentic
12	4.08	0.71	n.d.	adulterated
13	63.97	1.58	n.d.	adulterated
14	4.84	4.42	n.d.	adulterated
15	27.38	3.45	1.40	adulterated
16	43.46	a	n.d.	adulterated
17	67.25	a	n.d.	adulterated
Instant coffee produced in Czech Republic				
18	1.21	0.35	n.d.	authentic
19	2.72	1.11	0.13	adulterated

a – common peak with glucose
n.d. – not detected

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Abstrakt

BOHAČENKO I., VESELÝ Z. (2000): **Průkaz autenticity čisté instantní kávy**. Czech J. Food Sci., **18**: 165–169.

Pro stanovení limitních obsahů markerových sacharidů (volného manitolu a celkové glukosy, resp. xylosy) používaných pro průkaz autenticity čisté instantní kávy byla vypracována metoda HPLC s refraktometrickou detekcí. Tato metoda, i když je pracnější, poskytuje srovnatelné výsledky s metodou HPAE-PAD a je tedy určena především pro ty laboratoře, které i v současné době používají pro analýzu sacharidů běžnou techniku HPLC s refraktometrickou detekcí. V rámci průzkumu trhu bylo zjištěno, že k falšování dochází nejvíce u zahraničních druhů instantní kávy balených v ČR – ze sedmi vyšetřovaných vzorků pouze v jednom případě byla autentická káva. Naproti tomu u 10 vzorků instantních káv dovážených v originálním balení nesplňoval kritéria autenticity pouze jeden. Pokud se týká dvou vzorků instantní kávy domácí provenience, pak jeden z výrobců uvedl na trh kávu falšovanou a druhý autentickou.

Klíčová slova: instantní káva; autenticita; falšování; HPLC s RI detekcí

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