Determination of Silver in Ice Cream - Food Monitoring with Direct Solid Sampling HR-CS AAS

The bactericidal effect of silver has been known for a long time. As early as the 19th century, physicians used silver to treat wounds and for disinfection purposes. Its use for disinfecting drinking water can even be traced back to pre-Christian times - the custom to throw coins into the well did not simply promise good fortune but also improved water quality. Moreover, people added a silver coin to their milk cans for a long time to keep the milk fresh over longer periods. With the development of fridges, disinfectants and antibiotics the antimicrobial effect of silver was all but forgotten. It has only been recently that its advantages are being rediscovered and are valued in many areas of application. Today, silver is used as a bactericide mostly in colloidal or ionic form, but also in form of coatings or nanoparticles, that are, for example, incorporated in clothing, utility items, medical tubes, instruments and wound dressings, but also in filter cartridges for water purification. The NASA Spaceshuttle uses silver for water purification purposes as well.

The bactericidal effect is based on several mechanisms. Silver inhibits the cell division and the transportation of nutrients in the cell and destabilises cell walls and membranes. This is a safe way to kill even bacterial strains that are resistant to antibiotics.

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In dairy production, sterile processing is particularly important, because dairy products are an ideal breeding ground for bacteria. This is why milk processing companies are regularly inspected by the responsible surveillance authorities. The main focus is on the microbiological control of the products, an indicator that the production equipment has been cleaned and disinfected carefully. But even if the devices are disinfected thoroughly and the manufactured products are impeccable, any disinfectant residue must be removed completely after cleaning to avoid that they end up in the final product. To ensure this, the silver contained in the cleaning agents serves as a marker. If silver is detected in the product, this suggests that the disinfectant was not washed out completely and the equipment has not been cleaned carefully enough.

Since dairy products such as ice cream cannot be analysed directly with the usual analytical methods, an acid digestion of the samples must be carried out before they can be analysed with atom spectrometric methods. This type of digestion, however, which is usually achieved with microwave-supported digestion systems, restricts the sample throughput of a laboratory because only few samples can be processed at a time. In addition, the personnel and time requirements are relatively high, which means that only a few samples can be analysed over the course of a day.

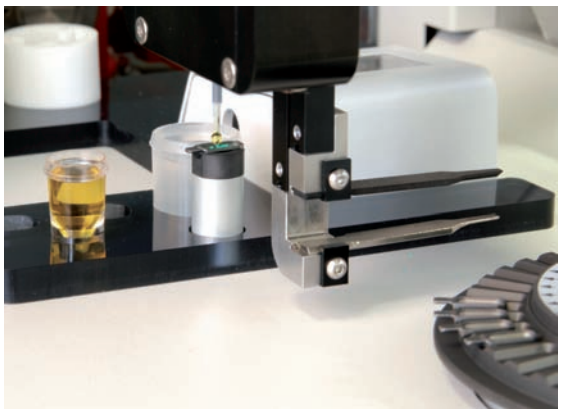

Figure 1. Fully automatic solid sampler SSA 600L with liquid option

SOLID AA® – A QUICK SCREENING METHOD

With the direct solids analysis with Graphite Furnace AAS the disadvantages of conventional sample preparation can be avoided. Solids, but also pasty substances, are supplied directly into the graphite tube and can be analysed straight away without any preparation. The fully automatic solid sampler SSA 600L *(Figure 1)*, which is available as an accessory for all Graphite Furnace systems from Analytik Jena, is the ideal tool for the automated analysis of up to 84 samples. Furthermore, the dilution of the sample, which would be inevitable for a digestion, can be avoided. Therefore, even the smallest silver concentrations can be detected with solid AA®.

A sample quantity of 15 – 20mg ice cream is placed on a special graphite sample carrier and then weighed in fully automatically on an integrated microbalance. The single-point calibration with an aqueous standard, the addition of an analyte modifier, in this case palladium nitrate, as well as the transport of the sample carrier into the graphite tube and back to the sample tray, are all carried out by the SSA 600L without any effort required by the user. The reusable sample carriers are immediately ready for the next analysis.

The temperature program of the graphite furnace *(Table 1)* replaces the previous mineralisation of organic sample matrices. After the sample has been dried carefully, organic components are removed by means of oxygen ashing. This is followed by the usual steps for pyrolysis, atomisation and clean-out.

Table 1. Temperature programme.

Step	Temp. [°C]	Ramp [°C/s]	Hold time [s]	Gas
Drying	120	6	15	Argon
Drying	150	5	15	Argon
Drying	200	5	15	Argon
Ashing	350	25	20	Argon-O2
Ashing	450	25	20	Argon-O2
Ashing	600	25	20	Argon-O2
Purge	600	0	10	Argon
Pyrolysis	850	100	10	Argon
Atomisation	2000	1200	4	Stop
Clean-out	2500	500	5	Argon

RESULTS

The direct determination of the silver content in ice cream by means of solid AA® serves as a quick, simple and sensitive screening method for official food control with which a large number of samples can be analysed in a short time. Samples with a noticeable silver content can be selected and tested more comprehensively without much effort.

Since dairy products are already homogenised during the production, even small random samples can be regarded as representative. Both single and duplicate measurements are thus sufficiently meaningful with regard to the quality of the product. The good reproducibility of a tenfold measurement supports this *(Table 2)*. The high measurement sensitivity of the procedure allows precise determination in the µg/kg range *(Table 3)*, the high sample throughput allows an uninterrupted monitoring of the sampled manufacturers.

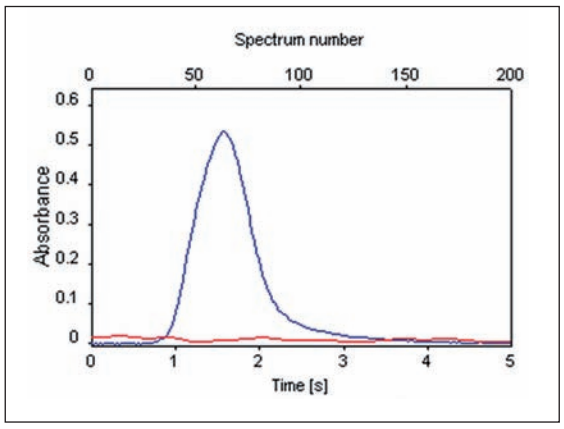

Figure 2a. Signal profile standard solution 500pg Ag

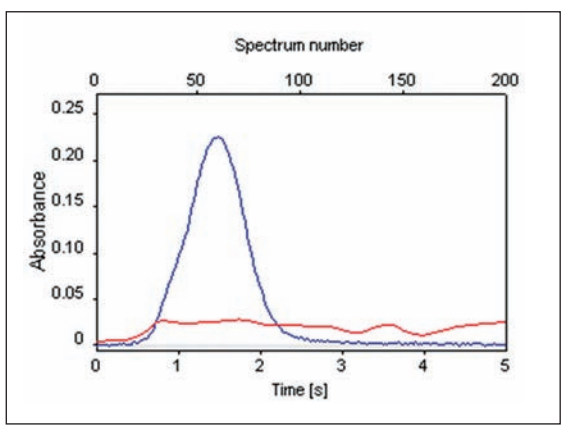

Figure 2b. Signal profile pistachio ice cream (12.3µg/kg)

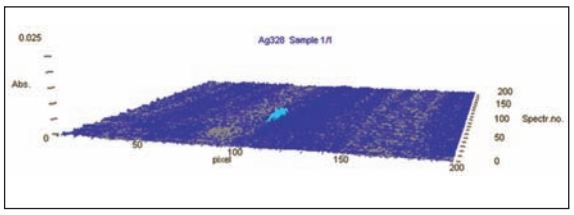

Figure 3a. 3D spectrum vanilla ice cream (1.7µg/kg)

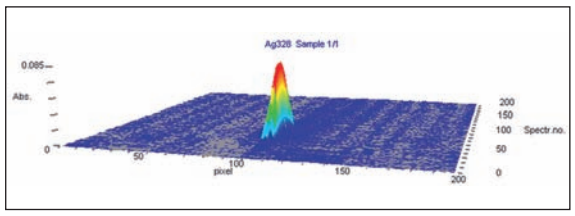

Figure 3b. 3D spectrum pistachio ice cream (12.3µg/kg)

The signal profiles *(Figure 2)* and the time and wavelength-resolved 3D absorption spectra *(Figure 3)* of the samples do not exhibit any spectral interferences. The absence of non-spectral interferences and therefore the accuracy of the method was confirmed with the help of spiked samples *(Table 3)*.

The direct solid analysis with Graphite Furnace AAS thus proves to be a quick, simple and sensitive screening method for this application. The High-Resolution Continuum Source AAS allows unlimited flexibility for the element and wavelength selection, because instead of an element-specific radiation source, a continuum radiator is used here, that covers the whole spectral range relevant in the AAS. The use of a high-resolution spectrometer and a CCD line detector allows the time and wavelength-resolved display and evaluation of the absorption spectra of the sample for the first time in AAS. Spectral interferences can be detected straight away and corrected if necessary.

Figure 4. contrAA 700 – High-Resolution Continuum Source AAS with SSA 600

Table 2. Reproducibility of direct silver detection.

Sample	Concentration [µg/kg]	RSD [%], n=10
Pistachio ice cream	12,3	4,8

Table 3. Measurement results and accuracy of some ice cream samples.

Sample	Concentration [µg/kg]	Recovery rate [%]
Vanilla ice cream	1,7	
Vanilla ice cream + 10 µg/kg	12,4	107
Lemon ice cream	< 0,5	
Lemon ice cream + 10 µg/kg	9,7	97
Chocolate ice cream	8,9	

Food Safety Application Notebook

The **Dionex** Food Safety Application Notebook, a 170-page plus compilation of food safety applications in an easy-to-use PDF, is available on the Dionex website. Concerns about food safety have risen to the forefront with the frequent exposés of dangerous and, sometimes, deadly contamination in the global food supply chain in the last few years. Products are grown and processed in widely differing environments under a variety of regulatory frameworks, travel thousands of miles, are kept in various storage conditions, experience temperature fluctuations that may affect shelf life, and are handled by many different people. At any point in this process, products can be contaminated or may become unfit for consumption.

Dionex has been working with industry and regulatory agencies to develop numerous extraction, sample preparation, IC, and HPLC solutions for the determination of a broad range of food contaminants so that many of these food contaminants can be isolated and identified reliably and quickly before they reach the table. The Dionex Food Safety Application Notebook lists and describes food safety applications grouped by contaminant type: agricultural, chemical, environmental, food additive, and food processing. Applications include pesticides through acrylamide in foodstuff. The notebook combines applications notes on extraction and analysis by HPLC or IC and includes a Column Selection Guide.

Circle no. 131

Increased Awareness of E. coli O26

Rhamnose MacConkey (VTEC O26) Agar from microbiology specialist **Lab M**, is selective for verocytotoxin producing Escherichia coli O26. An established pathogen, this strain is linked to outbreaks of haemorrhagic colitis (HC) and haemolytic uraemic syndrome (HUS).

In addition to the need for comprehensive health and safety monitoring in the food industry, increased awareness of the VTEC O26 strain in both clinical and veterinary settings has coincided with the development of microbiological techniques that have improved detection and characterisation of this pathogen.

Lab M's Rhamnose MacConkey (VTEC O26) agar is based on traditional MacConkey medium but with rhamnose substituted as the fermentable carbohydrate in place of the usual lactose. Unable to ferment the rhamnose present in the medium, E. coli O26 colonies remain translucent. All non-O26 VTEC colonies will be pink to red. Selectivity of the medium can be increased further by adding X161 Cefixime Tellurite (CT) supplement.

Using Lab M's highly selective Rhamnose MacConkey (VTEC O26) agar, detection and identification is now straightforward, enabling both effective monitoring within food industry environments and further understanding of the consequences of its presence in clinical and veterinary settings.

Circle no. 132

Multi-Residue Analysis of Pesticides in Rice

Thermo Fisher Scientific, Inc announced a new method that enables rapid and accurate identification and quantification of pesticides in rice. The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction method takes advantage of the Thermo Scientific ITQ 700 GC-ion trap mass spectrometer and the Thermo Scientific FOCUS GC gas chromatograph to increase speed and improve sample preparation. The application note describing the method, entitled 'Multi-residue Pesticide Analysis in Rice by a Modified QuEChERS Extraction and Ion Trap GC/MSn Analysis'.

Recently formulated pesticides are smaller in molecular weight than their predecessors and are designed to break down rapidly in the environment. As a result, more careful consideration must be placed on the sample preparation for extraction and the instrument parameters for analysis in order to successfully identify and quantify these compounds in foods. The QuEChERS sample preparation method, which is already shown to simplify the determination of pesticides in fruits, vegetable, grains and herbs, can now be used to successfully prepare rice extracts before ion trap GC/MSn analysis.

The study was performed by pairing the ITQ 700 with the Thermo Scientific FOCUS GC gas chromatograph to establish the linear ranges, quantitation limits and detection limits for a list of pesticides that are commonly used on rice crops. Samples were prepared in matrix using the QuEChERS sample preparation method, which involves extraction, clean up and solvent exchange processes. The ITQ 700 GC-ion trap MS demonstrated excellent accuracy at low concentrations of 33 pesticide residues analysed in rice. The optional MSn mode was shown to offer enhanced selectivity over scanning modes such as full scan and selected ion monitoring (SIM). This enables users to identify, confirm and quantify the existence of pesticides in a single analytical run. In addition, the daily analysis of endrin, DDT and their breakdown products confirmed the system's ability to analyse active compounds without the need for continual, expensive and time-consuming maintenance.

Circle no. 133