

Sodium Determination

A Comparative Study

Sodium determination is becoming ever more important in the food industry. Sodium is an essential ingredient in processed foods, but too much can be detrimental to health. Direct sodium measurement is commonly performed e.g. by atomic absorption spectroscopy (AAS), ion chromatography (IC) or inductively coupled plasma mass spectroscopy (ICP-MS). However, in addition to tedious sample preparation and time-consuming system calibration procedures, these techniques require significant capital investment and in-depth user knowledge. Among these techniques, the multiple standard addition (MSA) technique on METTLER TOLEDO's Titration instruments represents a simpler, faster and economic application to specifically and accurately determine the content of sodium ions in food products.

This White Paper describes a comparative study of the multiple standard addition (MSA) method with respect to AAS, IC and ICP-MS techniques for the content determination of sodium in various food samples. AAS, IC and ICP-MS measurements were carried out by the internationally recognized testing laboratory Swiss Quality Testing Services (SQTS).

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1. Multiple standard addition technique (MSA): Principle

Sodium determination using multiple standard addition technique is performed by ion-selective sensors. Briefly, small amounts of sodium standard solution (dV_s) of known concentration are added to the sample solution in multiple incremental steps (figure 1). The addition of the standard solution increments increases the sodium concentration (c_s) within the sample as well as its volume. The differences in potential (dE) resulting from added standard increments of known volumes (dV_s) are used to determine the sample concentration directly by using an iterative evaluation algorithm based on the Nernst equation leading to a linear regression of the measured values (see figure 1).

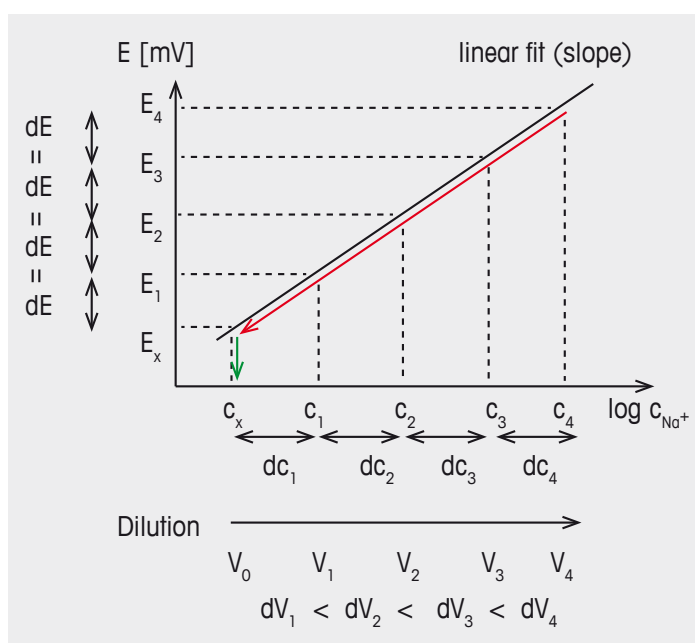


Figure 1: Principle of multiple standard addition technique.

Multiple standard addition technique reduces matrix effects because the calibration values are obtained in the presence of the sample during the sodium determination itself. As a result, this method allows for determination of sodium content in a wide variety of non-homogeneous samples including fatty snacks, meat and hard cheeses.

2. Scope of the comparative study

Six different food products were analyzed for their sodium content by means of METTLER TOLEDO Titration Excellence at Market Support Group Analytical Chemistry (MSG AnaChem in Schwerzenbach, Switzerland) and by AAS, IC and ICP-MS techniques at Swiss Quality Testing Laboratory (SQTS in Dietikon, Switzerland). Analyses for all techniques were performed in triplicate.

Food samples:

- cacao powder
- milk
- salad dressing
- cornflakes
- cheese
- meat

3. Sample preparation and measurement

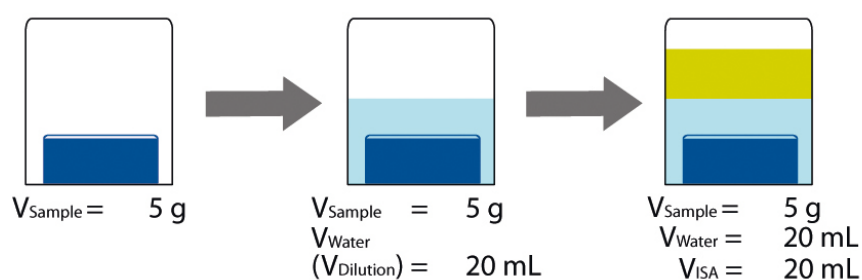
3.1 Multiple standard addition (MSA) technique

Sample preparation:

Sample quantification is performed in an aqueous solution which is obtained by dissolving and/or diluting a known amount of sample in a known volume of solvent:

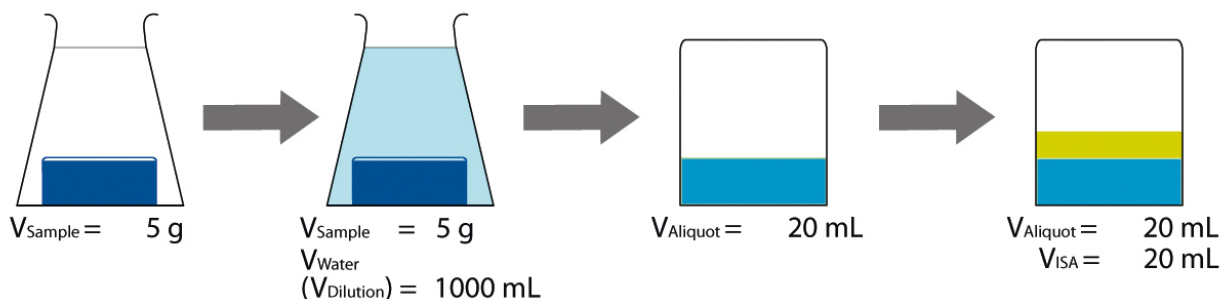
- Direct sampling for milk and salad dressing sample:

Direct sampling is used for homogeneous and/or liquid samples. The samples may be used directly or ground. Samples are transferred directly into the analysis beaker by accurate pipetting or weighing. Water and Ionic Strength Adjustment (ISA) solution are added.



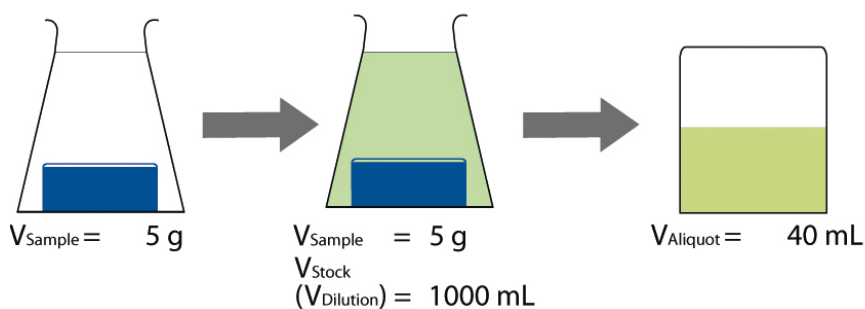
- Dilution solution "aliquot excluding ISA" for cornflakes, cheese and meat sample:

For non-homogeneous samples, a so-called dilution solution is prepared. A large amount of sample is first weighed into a volumetric flask. The flask is then filled up to the mark with deionized water. This dilution solution is mixed thoroughly for a few minutes. An aliquot is pipetted into the analysis beaker and ISA solution is added to the solution.



- Dilution solution "aliquot including ISA" for cacao powder sample:

For non-homogeneous samples that do not dissolve well in water, a dilution solution consisting of deionized water and ISA solution is used. For the measurement, an aliquot of this dilution solution is pipetted accurately into the analysis beaker.



Measurement:

Select the method parameters and sample size in order to be able to work within the optimum method parameter range:

- Potential difference (dE) to be achieved and number of additions to be chosen for a total potential difference E_{total} covering 30–100 mV:
 1. dE: 6 mV–12 mV
 2. No. of increment additions: 4–6
- Total consumption of 4–14 mL when using the 2000 ppm sodium standard solution

Sample	Sample preparation technique	Sample size	dE	Nr of additions	Sodium standard solution
Cacao	Aliquot incl. ISA*	15 g	12 mV	5	2000 ppm
Milk	Direct	2 mL	10 mV	5	2000 ppm
Dressing	Direct	0.4 g	10 mV	5	2000 ppm
Cornflakes	Aliquot excl. ISA*	4 g	10 mV	5	2000 ppm
Cheese	Aliquot excl. ISA*	5 g	10 mV	5	2000 ppm
Meat	Aliquot excl. ISA*	2.5 g	10 mV	5	2000 ppm

* the given sample size is used for a total dilution volume of 500 mL.

Table 1: Sample preparation and method parameters used for the different food samples.

3.2 Ion chromatography (IC)

Sample preparation:

Since most samples are not in a form that can be directly injected in the analytical instrument, a specific sample preparation step is required for every sample. In case of complex matrices carrying high organic loads such as dairy products, a more extensive sample preparation is mandatory to prevent damage of the chromatographic column. Furthermore, the analyte has to be in ionic form and dissolved in solution without the presence of interfering substances. For cation analysis, dilution is generally achieved with nitric acid (HNO_3).

For the six different food samples, the organic substances which could interfere with the analyses or harm the chromatographic column, were removed by ashing during several hours at 550 °C. The ash was then diluted in 2 mL nitric acid (65% HNO_3). The nitric acid was afterwards evaporated during 30 minutes in a water bath. The residue was further dissolved in 1 mL nitric acid ($c(\text{HNO}_3) = 0.25 \text{ mol/L}$) and filled up to 50 mL.

Measurement:

The sample solution (10 μL) is injected into the separation column. A measurement time of 30 minutes per sample is required. A calibration curve needed for the quantification of the specific ion in the sample solution is obtained by using external reference standards. The peak areas are proportional to the known amounts of external standard. Identification of the corresponding ion is carried out by confirming that the same retention time as for the standard solution is obtained.

3.3 Atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectroscopy (ICP-MS)

Sample preparation:

The sample may be homogenized if necessary. Concentrated $\text{HNO}_3/\text{H}_2\text{O}_2$ is added and the sample is digested in the microwave for 20 minutes. The sample is cooled down to room temperature and diluted with deionized water to a predefined volume.

Measurement:

The sampled material is introduced in a high-energy argon plasma (ICP) or a flame or graphite furnace (AAS) for excitation and atomization. Concentrations are quantified using a calibration curve achieved by measuring external reference standards.

4. Results

Table 2 provides the results of sodium content determination for six different food products. The food samples have been analyzed by multiple standard addition using METTLER TOLEDO Titration Excellence at Market Support Group Analytical Chemistry (MSG AnaChem), and by AAS, IC and ICP-MS techniques at Swiss Quality Testing Laboratory SQTS. Analyses for all techniques have been performed in triplicate.

Sample	Declaration [mg/L]	Multiple standard addition		AAS		IC		ICP-MS	
		content [mg/L]	n=3 s _{rel} [%]	content [mg/L]	n=3 s _{rel} [%]	content [mg/L]	n=3 s _{rel} [%]	content [mg/L]	n=3 s _{rel} [%]
Cacao	400	205 ± 7	3.4	209 ± 9	4.1	230 ± 7	3.1	260 ± 7	2.6
Milk	500	387 ± 2	0.5	381 ± 8	2.0	270 ± 11	4.1	340 ± 19	5.6
Dressing	5600	5419 ± 66	1.2	5238 ± 54	1.0	5500 ± 28	0.5	5700 ± 46	0.8
Cornflakes	7900	8133 ± 43	0.5	7855 ± 15	0.2	8200 ± 40	0.5	8200 ± 20	0.2
Cheese	12000	10396 ± 101	1.0	11047 ± 21	0.2	12000 ± 46	0.4	9900 ± 36	0.4
Meat	16000	16095 ± 87	0.5	15534 ± 57	0.4	16000 ± 100	0.6	13400 ± 39	0.3

Table 2: Sodium result comparison between the multiple standard addition, AAS, IC and ICP-MS method performed by SQTS testing laboratory.

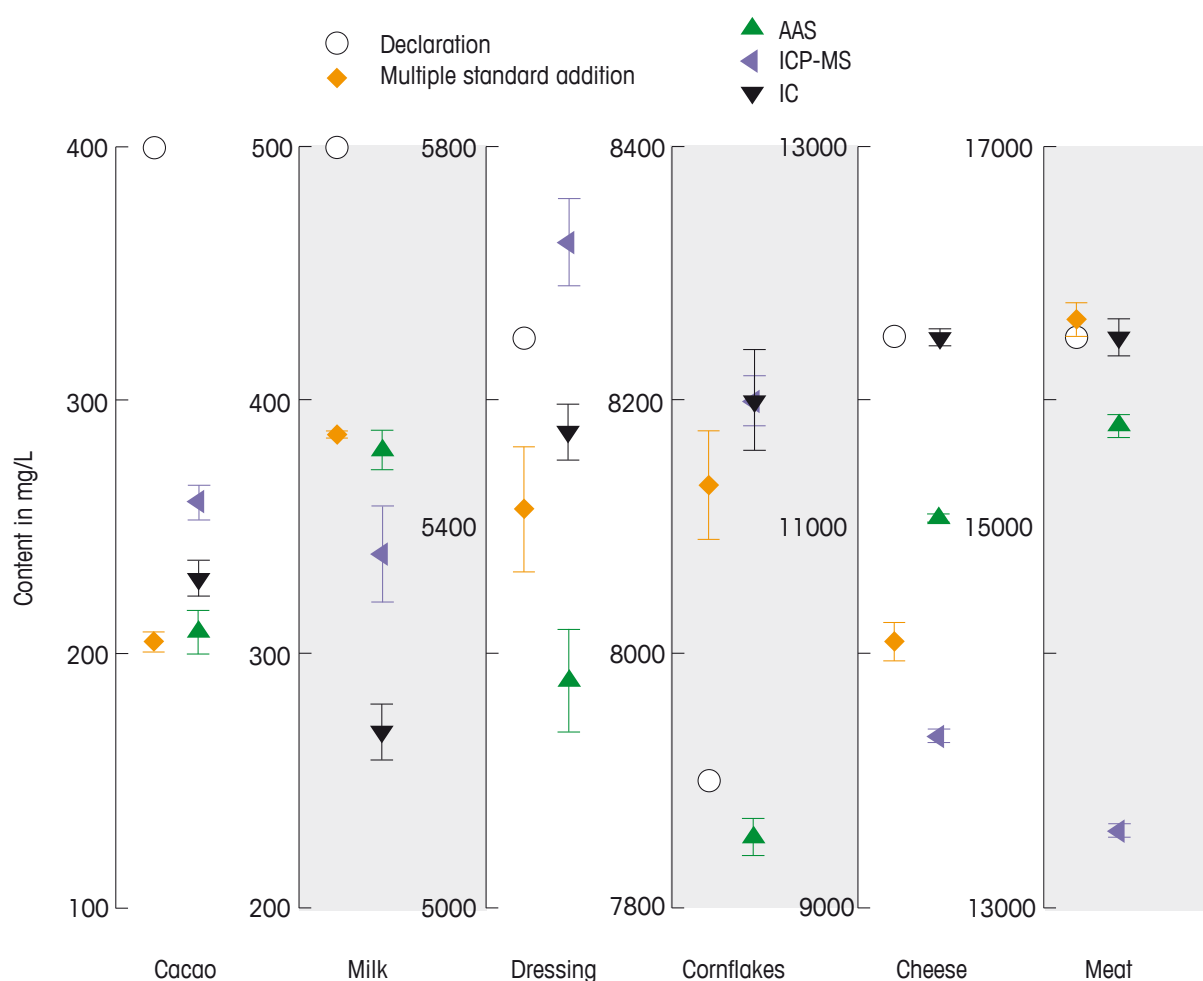


Figure 2: Display of the sodium content results obtained using multiple standard addition and conventional techniques AAS, IC and ICP-MS together with the theoretical sodium content values.

For a better overview, comparison results are displayed in correlation in table 3, whereas the sodium content determination using multiple standard addition technique is taken as 100%.

Sample	Recovery [%] compared with multiple standard addition		
	AAS	IC	ICP-MS
Cacao	102.0	112.2	126.8
Milk	98.5	69.8	87.9
Dressing	96.7	101.5	105.2
Cornflakes	96.6	100.8	100.8
Cheese	106.3	115.4	95.2
Meat	96.5	99.4	83.3

Table 3: Recovery of the sodium determination of AAS, IC and ICP-MS compared to multiple standard addition technique.

For cacao powder, the sodium content determined by multiple standard addition shows a good agreement with the result obtained by AAS (see table 2, table 3 and figure 2). The conventional techniques AAS, IC and ICP-MS differ up to 25% from each other, with the largest difference between AAS and ICP-MS. Also for milk, multiple standard addition technique is best comparable with AAS, with a very good recovery rate of 98.5%. For both the cacao and the milk sample, the value declared on the food product label is higher than the sodium content measured using all four different techniques. Sodium content of these two samples is very low with 200 to 400 mg/L, which corresponds to 0.02 to 0.04 g/100 g. As samples with such low sodium contents are more prone to variations and deviations, the comparably high sodium declaration can be expected to be a safety measure in order not to exceed the declared value. For salad dressing sample, deviations between the different techniques are rather small with the highest difference of 8.8% between AAS and ICP-MS. The sodium content in salad dressing measured using multiple standard addition lies well within the range of the conventional techniques. For cornflakes sample, deviation between all the techniques is small, with the largest difference of only 4.4% between AAS and IC. The relative standard deviations (s_{rel}) are low for all the techniques, with values ranging between 0.2 and 0.5%. For cheese, a rather strong deviation with more than 20% difference can be observed between IC and ICP-MS. The result using the multiple standard addition technique lies well between the results of AAS and ICP-MS. For meat, ICP-MS measured a significantly lower sodium content than AAS, IC and multiple standard addition technique. The results achieved using multiple standard addition technique are well comparable to IC and AAS, with a recovery of 99.4 and 96.5%.

The results demonstrate both the high precision and the excellent recovery of the multiple standard addition technique compared to AAS, IC and ICP-MS methods (see table 3). Sodium content results obtained by means of multiple standard addition technique correlate very well with the results achieved using AAS (see figure 2 and table 3). Indicating that with both analytical techniques, sodium ions can be successfully released completely from the sample matrix and are subsequently properly measured. Out of all the tested direct techniques for sodium determination, ICP-MS is the analytical method leading to results that differ the most from the other techniques.

The relative standard deviations (s_{rel}) achieved using multiple standard addition technique for sodium determination are comparable to those obtained using AAS, IC, ICP-MS analytical techniques. The relative standard deviation obtained with multiple standard addition method is small with values ranging from 0.5 to 1.2%, for cornflakes and salad dressing sample, respectively. For samples of low sodium content like cacao powder and milk sample higher relative standard deviations have to be expected for all of the techniques.

5. Conclusion

Multiple standard addition was successfully applied to measure the sodium content of several food samples. This technique was compared with AAS, IC and ICP-MS techniques.

The outcome of the comparison of the results obtained at the testing laboratory SQTs shows that the multiple standard addition technique correlates very well to the established techniques AAS, IC and ICP-MS. Furthermore, sample preparation for the multiple standard addition is straightforward. No complex and long-lasting sample preparation steps as required by the conventional techniques is necessary. Moreover, in contrast to the conventional analytical techniques, no external calibration procedure is needed, as the calibration curve is directly contained in the sample measurement. The measurement procedure itself is straightforward and does not require in-depth knowledge from the operator and can be started with OneClick™.

METTLER TOLEDO offers several solutions for this simple and effective technique. It goes from the stand-alone Sodium Analyzer with manual sample preparation to a fully automated system with automatic sample preparation and sensor cleaning with Titration Excellence in combination with InMotion Autosampler.

For more information about the multiple standard addition technique and instrumental possibilities, please visit:

► www.mt.com/sodium-determination

www.mt.com

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