Food Authenticity Testing by Strontium Isotope Ratio Determination in Wine and Cereals Using ICP-MS

Challenge

Best isotope ratio precision ($^{87}Sr/^{86}Sr$) to allow for the discrimination of food (cereals) and beverage (wines) matrices.

Solution

PlasmaQuant MS Elite with a 90° ion mirror, a high-definition quadrupole, and a full digital detector for accurate measurements of a wide range of signal intensities to obtain the best isotope ratio precision.

Introduction

Food authenticity is defined as "the process of irrefutably proving that a food or food ingredient is in its original, genuine, verifiable and intended form as declared and represented" [1] by the International Food Authenticity Assurance Organization (IFAAO). The determination of food authenticity is a topic of increasing importance for food quality control laboratories for several reasons. The occurrence of diseases associated with a food product originating from a particular region makes it necessary to be able to control the origin to ensure consumer safety. Furthermore, certain agricultural products and foodstuffs are produced, processed, and/or prepared in a specific geographical region with a recognized quality standard. This has led to the creation of different quality labels, such as Protected Designation of Origin within the European Union. The products bearing these labels are more valued by customers, which is often reflected in a significantly higher price compared to otherwise similar products. In these cases, it is necessary to ensure that any mislabeling or false information about the origin of a particular product, or adulteration resulting from the incorporation of substances of inferior or unrecognized quality, can be detected and reported to the relevant authorities.

Chemical analysis plays a crucial role in this type of forensic work. A wide variety of techniques can be applied to a range of food products to develop methods that will permit their geographical origins to be determined with varying degrees

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of certainty.[2,3] Measuring elemental concentrations and isotopic variation in premium regional products is arguably the best analytical strategy for accurately verifying geographical origin. There are several recognized analytical approaches to determine the geographical origin of foods, for example based on the determination of elemental composition, organic components, stable isotopes ratios of light elements, and genetics. The use of isotope ratios of certain elements, such as lead (Pb) and strontium (Sr), is a relatively new approach. These two elements have radiogenic isotopes. Thus, the soil and rocks of different geographical areas where agricultural products are cultivated may show significant variations in their isotopic signatures. If these differences are preserved throughout the whole production chain, it may be possible to use them to determine whether certain ingredients truly originate from a particular geographic area.

The product that has attracted the most attention in isotope ratio research, and was the first to be studied, is wine.[3] Quality and prices of wine are strongly linked to the area of grape collection and the wine production itself. The $^{87}Sr/^{86}Sr$ ratio has shown to be a useful tool for the designation of origin. In addition to wine, other food products have been similarly studied in recent years, further confirming the use of $^{87}Sr/^{86}Sr$ ratios for this purpose.
The $^{87}Sr/^{86}Sr$ isotope ratio can therefore be considered as a parameter allowing for the discrimination of wines of different origin, provided that precise and accurate measurements are performed[4]. Indeed, a difference of 0.03% was reported between the Amselfeder and the Valpolicella wines[5] and of 0.08% between the Côtes du Rhône and the Vallée du Rhône wines.[6] Therefore, a minimum precision of 0.01% is recommended.
Such precision (a value of 0.004% on a routine basis was quoted) is reached with thermal ionization mass spectrometry (TIMS)[5,6], which is a widely established tool in geochemistry. The analytical procedure required to purify the element of interest before measurement, is, however, tedious and cumbersome. The higher matrix tolerance of the ICP-MS technique offers a significant benefit in terms of sample preparation, increasing the popularity of using ICP-MS to obtain trace element and isotopic information. However, the lack of precision of Q-ICP-MS, typically around 0.1%, is a considerable limiting factor in studies involving the measurement of the $^{87}Sr/^{86}Sr$ isotope ratio.[7,8]
An improved precision (0.002–0.003%) was obtained by ICP-Sector Field (SF)-MS for the determination of the $^{87}Sr/^{86}Sr$ isotope ratio in wine.[9] The precision of isotope ratio measurements in ICP-SF-MS can also be improved using a multi-collection detection (MC).
This application note shows the capabilities of the PlasmaQuant MS Elite for the determination of the $^{87}Sr/^{86}Sr$ isotope ratio in wines and cereals in comparison to MC-ICP-MS. The ability to differentiate the origin of the food products is shown.

Materials and Methods

Instrumentation

For the Sr elemental quantification analysis and Sr isotope ratio determination, a Q-ICP-MS PlasmaQuant MS Elite (Analytik Jena, Germany) was used in a no gas operation mode. For comparison purposes, a MC-ICP-MS Nu Plasma (Nu Instruments Ltd., UK) was used. All experiments were carried out using standard environmental conditions at the Advanced Isotopic Analysis (AIA) Laboratory in Pau, France. The PlasmaQuant MS Elite operating conditions are listed in Table 1.

Table 1: PlasmaQuant MS Elite operating conditions

Parameter	Specification
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.35 L/min
Sheath gas flow	0.00 L/min
Nebulizer gas flow	1.15 L/min
iCRC condition	No gas
Plasma RF power	1.40 kW
Dwell times	^{83}Kr – 3,000 µs ^{86}Sr – 9,000 µs ^{87}Sr – 10,000 µs ^{88}Sr – 3,000 µs ^{85}Rb – 3,000 µs
Scans per replicate	400 (peak hopping mode, 1 pt/peak)

Parameter	Specification
No. of replicates	30
Pump rate	14 rpm – black/black PVC pump tubing
Sample uptake time	120 s
Stabilization delay	30 s
Sampling depth	5.0 mm
Nebulizer type	MicroMist™ (quartz concentric)
Ion optics	Auto optimized
Spray chamber type	Glass Scott
Spray chamber temperature	3 °C

Samples and Reagents

The following high-purity reagents were used for all solution preparations:

- HNO_3 (69.0–70.0%, Optima, Fisher Chemical, Fisher Scientific, France)
- Ultrapure water obtained from the Milli-Q system (resistivity of 18.2 MΩ cm, Veolia Water Technologies, France)
- Hydrogen peroxide H_2O_2 (30%, Optima, Fisher Chemical, Fisher Scientific, France)
- Sr isotopic standard reference material SRM 987 (pure $SrCO_3$, NIST, U.S.)

Sample Preparation

Sample preparation for Sr isotopic analysis consisted of digestion steps followed by the matrix separation with Sr. To ensure quality control, several procedural blanks were prepared using the same procedure.
A variety of cereals (5 types of wheat and 3 types of quinoa) were digested in a TOPwave microwave digestion system (Analytik Jena, Germany) using the settings displayed in Table 2. Wines were digested on a Hotblock system (Environmental Express, U.S.). All samples had a clear transparent appearance after microwave digestion and were ready for the matrix separation step before the isotopic analysis.

Table 2: Digestion method parameters used on the TOPwave microwave system for cereals and on Hotblock for wines

Parameter	Specification for cereals	Specification for wines
Sample amount	0.5 g	1 mL
HNO_3 volume	5 mL	1 mL
H_2O_2 volume	2 mL	0.5 mL
Vessel type	PM60	PP tubes
Heating stage 1 / ramp time	170 °C / 10 min	85°C for 4 hours with HNO_3 After adding H_2O_2, 85° for 3 hours
Heating stage 2 / ramp time	260 °C / 25 min	
Heating stage 3 / holding time	260 °C / 25 min	
Cooling / time	50 °C / 30 min	
Final volume	50 mL with ultrapure H_2O	

A precise and accurate determination of Sr isotope ratios by MC-ICP-MS and Q-ICP-MS requires a separation of Sr from the sample matrix, specifically from Rb, which produces an isobaric interference of ^{87}Rb on ^{87}Sr. The following procedure was applied: the aliquots of digested wine/cereal samples with an approximate content of 2–2.5 µg of Sr (necessary amount for a reliable isotopic ratio determination) were evaporated to dryness in 30 mL Savillex vials using an EvapoClean (Analab, France) at 100 °C and re-dissolved in 4 mL of 3 mol L^{-1} HNO_3. An amount of 130 mg of the Eichrom Sr-selective resin was put into a 2 mL column fitted with appropriate filters to fix the resin inside the column to ensure a slow and constant flow rate of about 0.5 mL min^{-1} required to obtain an acceptable recovery rate. At first, to avoid any contamination, the packed resin was prewashed with 5 mL of 3 mol L^{-1} HNO_3 and rinsed with 20 mL of ultrapure water. Then, the resin was conditioned with 2 mL of 3 mol L^{-1} HNO_3 to ensure the binding groups' sufficient activation. Next, the re-dissolved samples were loaded into the columns. The matrix removal was accomplished by flushing each column twice with 4 mL of 3 mol L^{-1} HNO_3. Finally, the Sr elution was obtained by rinsing the columns with 10 mL of ultrapure water. The resulting solutions were acidified to 2% HNO_3 (v/v) and contained a Sr concentration of around 200 µg.L^{-1}, and were ready to be analyzed by MC-ICP-MS and Q-ICP-MS after appropriate dilution. The concentrations of Sr and Rb in wine/cereal samples and procedural blanks were controlled using a Q-ICP-MS before and after Sr/matrix separation. The Sr recoveries obtained for samples were in the range of 90–105%. In addition, to ensure the quality of the separation, the Sr isotopic standard NIST 987 was prepared according to the same Sr separation procedure.

Strontium Isotope Ratios Analysis

The operating parameters of the MC-ICP-MS and Q-ICP-MS were optimized daily using the NIST SRM 987 standard solution with a concentration of 200 µg L^{-1} and 4 µg L^{-1}, respectively, to achieve maximum sensitivity and stability of the Sr signal. The typical signal for the ^{88}Sr isotope was about 7 V for MC-ICP-MS and 3.0 Mcps for Q-ICP-MS.
Measurements were performed using a conventional Sample-Standard Bracketing (SSB) calibration sequence with the NIST SRM 897 used as bracketing standard. After the instrumental blank was subtracted, the $^{87}Sr/^{86}Sr$ ratio was corrected for mass bias using the constant $^{87}Sr/^{86}Sr$ ratio of 0.1194, and from the potential remaining interferences from traces of ^{87}Rb using the $^{85}Rb/^{87}Rb$ ratio of 2.5926. A second correction was then applied regarding the standard bracketing. The value of the $^{87}Sr/^{86}Sr$ ratio for NIST SRM 987 applied for data processing was 0.710255 according to Waight T. et al.[10] For Q-ICP-MS, a supplementary correction can be applied with ^{83}Kr which can produce an isobaric interference on ^{86}Sr.
Without evaluation of the best acquisition parameters (e.g., dwell times, scans, and replicates), a precision of 0.04% for $^{87}Sr/^{86}Sr$ for the Q-ICP-MS was achieved by conventional SSB sequence using the NIST SRM 987 combined with instrumental blank subtraction and Rb/Kr corrections.

Evaluation of the Dwell Times, Number of Scans, and Replicates

A systematic evaluation of the influence of the data acquisition parameters on the isotope ratio precision was conducted to achieve the optimum conditions. For this purpose, the precision [RSD (%)] of the isotope ratio $^{87}Sr/^{86}Sr$ was evaluated using different combinations of dwell times of Sr isotopes, 400 scans, and 30 replicates (Table 3).
Dwell times were set according to the formula:

$$Dwell\ time\ (^{xx}Sr) = Dwell\ time\ (^{88}Sr) \times \sqrt{\%(^{88}Sr)/\%(^{xx}Sr)}$$

where $\%(^{xx}Sr)$ and $\%(^{88}Sr)$ are the natural abundances of Sr isotopes.[11]

Table 3: Dwell times in µs for Sr, Rb, and Kr isotopes

Option	Dwell time [µs]					Total estimated time [s]
	^{88}Sr	^{86}Sr	^{87}Sr	^{85}Rb	^{83}Kr	
1	500	1,500	1,700	500	500	330
2	1,000	3,000	3,500	1,000	1,000	387
3	2,000	6,000	7,000	2,000	2,000	501
4	3,000	9,000	10,000	3,000	3,000	609
5	5,000	15,000	17,000	5,000	5,000	837

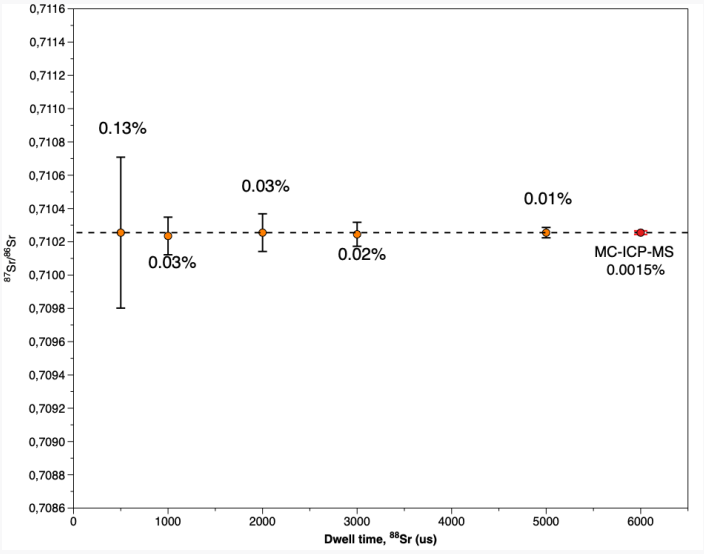

Figure 1: %RSD of $^{87}Sr/^{86}Sr$ vs. ^{88}Sr dwell time for NIST SRM 987. Error bars are 1*SD

As can be expected according to Poisson counting statistics, the isotope ratio precision significantly improves when increasing the measurement time (Figure 1). The PlasmaQuant MS Elite can achieve a precision down to 0.01% for $^{87}Sr/^{86}Sr$. However, such a combination has a total estimated analysis time of 837 s. Therefore, in all further work, a compromise of approximately 600 s total measurement time per sample was used. Table 4 combines various numbers of scans and replicates to keep the total acquisition time of 10 min per sample.

Table 4: Number of scans and replicates for a dwell time of 3000 µs for ^{88}Sr

Option	Scans	Replicates	Ratio scans / replicates	Total estimated time [s]
1	999	12	80	525
2	600	20	30	609
3	400	30	13	609
4	200	50	4	525
5	100	99	1	521

Figure 2 shows a good compromise of precision and total acquisition time using a combination of 400 scans and 30 replicates, delivering a precision of 0.02% for $^{87}Sr/^{86}Sr$ in 10 min measuring time per sample.

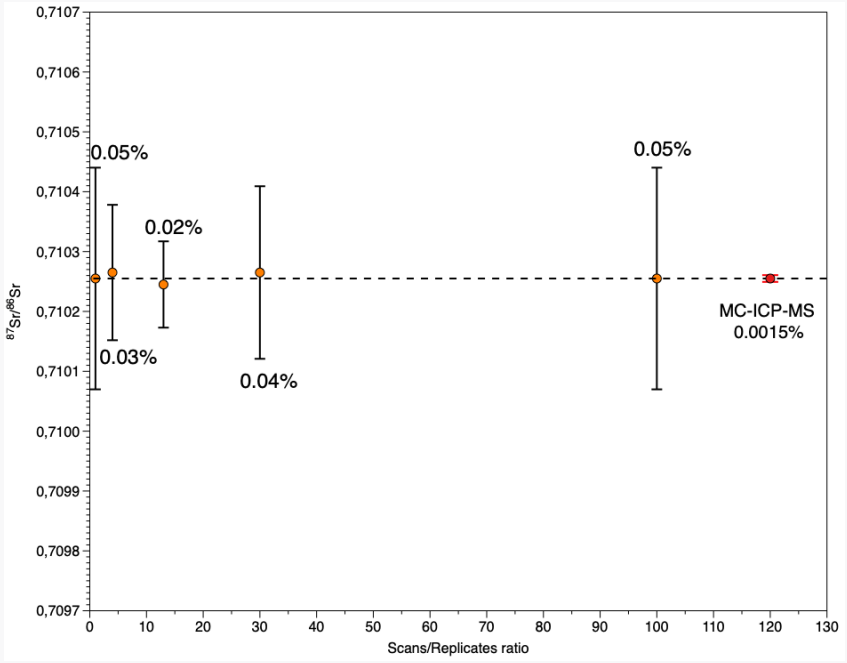

Figure 2: %RSD of $^{87}Sr/^{86}Sr$ vs. scans/replicates ratio for NIST SRM 957. Error bars are 1*SD

Long-term stability

Instrument stability was checked using the optimized conditions; a long-term stability test was carried out measuring the NIST SRM 987 over a period of four consecutive days without turning off the plasma (Figure 3).

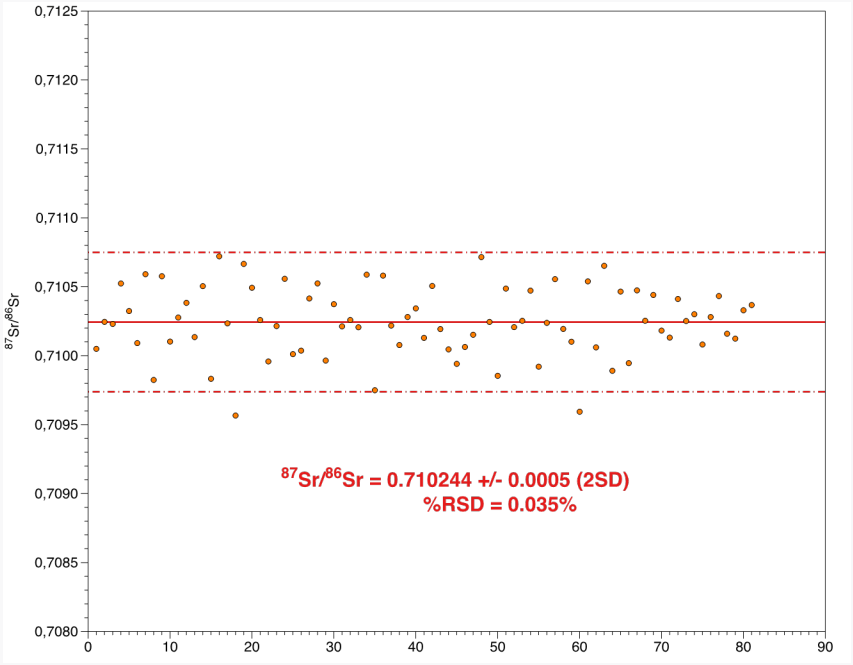

Figure 3: Long-term stability test (4 days) of NIST SRM 987. Interval bars represent 2*SD

Table 5: $^{87}Sr/^{86}Sr$ isotope ratios and precision for all samples measured by PlasmaQuant MS Elite and MC-ICP-MS

Sample ID	PlasmaQuant MS Elite				MC-ICP-MS			
	$^{87}Sr/^{86}Sr$	SD	%RSD	Overall precision %RSD*	$^{87}Sr/^{86}Sr$	SD	%RSD	Overall precision %RSD*
Quinoa 1	0.707094	0.0006	0.08		0.707061	0.00002	0.004	
Quinoa 2	0.711078	0.0006	0.08	0.08%	0.711168	0.00005	0.008	0.004%
Quinoa 3	0.704801	0.0006	0.08		0.704320	0.00002	0.002	
Wine 1	0.707773	0.0001	0.01		0.708127	0.00002	0.002	
Wine 2	0.708409	0.0002	0.02		0.708357	0.00002	0.002	
Wine 3	0.708468	0.0002	0.02	0.02%	0.708441	0.00002	0.002	0.002%
Wine 4	0.708532	0.0002	0.02		0.708452	0.00002	0.003	
Wine 5	0.708785	0.0002	0.02		0.708790	0.00002	0.003	
Wheat 1	0.710721	0.0001	0.02		0.710480	0.00002	0.002	
Wheat 2	0.709431	0.0001	0.02		0.709738	0.00002	0.002	
Wheat 3	0.709365	0.0001	0.02	0.02%	0.709256	0.00002	0.002	0.02%
Wheat 4	0.709618	0.0001	0.02		0.708852	0.00004	0.005	
Wheat 5	0.709195	0.0001	0.02		0.708984	0.00006	0.008	

* The overall precision was evaluated by preparing one of the samples of each matrix in triplicate and calculating the precision over these 3 replicates. Therefore, it includes the sample preparation and the analysis steps.

Results and Discussion

The $^{87}Sr/^{86}Sr$ isotope ratios were measured in various matrix types: quinoa, wine, and wheat. They are listed in Table 5 and graphically presented in Figure 4.

The precision obtained by the PlasmaQuant MS Elite ranged between 0.01 and 0.08% depending on the type of sample. The quinoa matrix provided the worst precision with 0.08%, but the highest variation for $^{87}Sr/^{86}Sr$ within the samples, which indicates different geographical origins. Wheat and wines showed lower %RSD of 0.01 to 0.02% and a smaller variation range for $^{87}Sr/^{86}Sr$ than quinoa. However, due to the exceptional precision obtained, it was also possible to distinguish different origins in both types of samples.

An excellent correlation (Figure 4) was also achieved between the measurements carried out on the PlasmaQuant MS Elite and an MC-ICP-MS. This demonstrates the accuracy of measurement of the PlasmaQuant MS Elite.

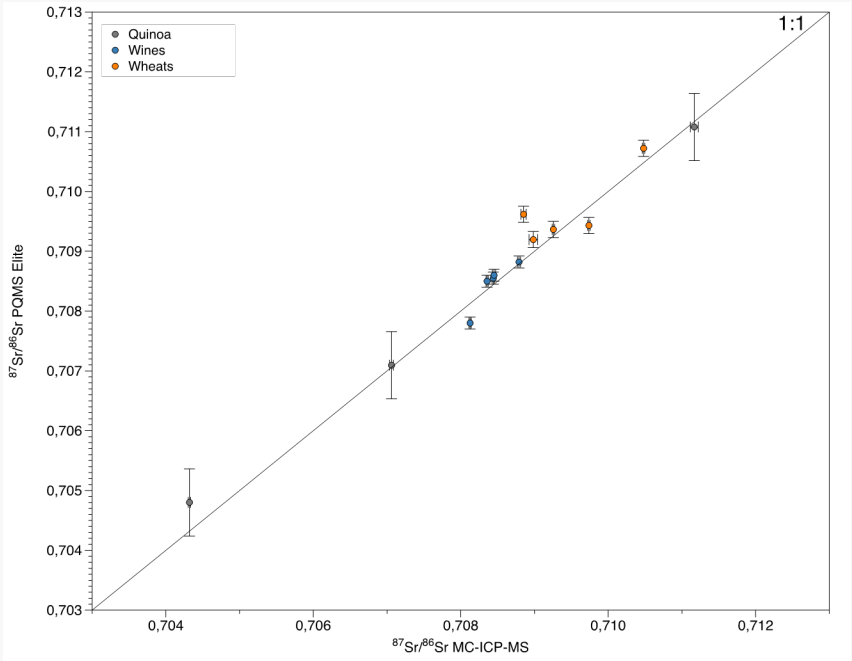

Figure 4: Correlation between $^{87}Sr/^{86}Sr$ isotope ratios for all samples measured by PlasmaQuant MS Elite versus MC-ICP-MS. Error bars are 1*SD

Conclusion

Although the $^{87}Sr/^{86}Sr$ ratio precision obtained by the PlasmaQuant MS Elite of 0.01% is significantly poorer than that obtained with MC-ICP-MS (0.0015%), this application note showed by far superior analytical performance compared to other Q-ICP-MS instruments (0.1%) used for this purpose. The results of the measured samples have shown that a relevant origin discrimination can be derived from PlasmaQuant MS Elite measurements. The case study clearly demonstrates the benefit of using the PlasmaQuant MS Elite for food authenticity studies in cases where the expected variation in the $^{87}Sr/^{86}Sr$ ratio is greater than the analytical precision.

The main advantages of a Q-ICP-MS are a high sample throughput, straightforward sample introduction, and, especially, the wide availability of such instruments in geochemical and academia laboratories. For highly precise isotope ratios determinations, however, Q-ICP-MS cannot compete with TIMS, unless a MC-ICP-MS is used.

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