Application Note · PlasmaQuant MS

Lead Isotope Ratios in Cigars as a Tracer of Authenticity Using ICP-MS

Introduction

The authenticity of a product is an irrefutable guarantee of its high quality. Unfortunately, the appearance on the market of counterfeit products is quite frequent and generates economic losses. That is the case with cigars because most of them are high quality products. They are mainly produced in the Caribbean and South America. Cuban cigars have a worldwide recognition, and the Havana cigar is one of the best quoted trademarks on the international market. In addition, tobacco is part of the culture and identity of the Cuban nation. Preserving this distinction, the commercialization of this product occupies the fourth position among the most influential sector of the Cuban economy.

Several indicators have been implemented to ensure the authenticity of cigars based mainly on characteristics that can be counterfeited. However, new techniques are needed to address the weaknesses of the methods previously developed for authenticity. Plants accumulate trace metals from the soil, and they are deposited on the foliage. Since the elements are accumulated in the same isotopic ratios (IR) as they occur in the source soil, the IR reflects the sources and indicates the geographic origin of products derived from vegetative matter. [1] The following two techniques based on the IR have been used to determine the geographic origin of agricultural products: (1) isotope composition of "traditional" elements (H, C, N, O, S, etc.) and (2) isotope ratios of "non-traditional" elements (B, Sr, Pb, etc.).[2–5] Compared to "traditional" elements, isotopes of some "traditional" elements are rarely fractionated in the terrestrial ecosystem, and the latter are more advantageous for determining the geographic origin.[6]

Challenge

Achieve the best isotope ratio (IR) precision (^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb) to allow for the discrimination of origin of cigars.

Solution

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

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Establishing the IR database of a product helps to identify whether other new products belong to this category. The major fraction of lead in agricultural products originates from the soil and from secondary sources such as low amounts of the substances, pesticides, fertilizers, vehicle exhaust, etc. The isotopic composition of lead is of interest because ^{208}Pb, ^{207}Pb and ^{206}Pb are derived from the radioactive decay of ^{232}Th, ^{235}U and ^{238}U, respectively.[7] Large variations in lead IR are observed in environmental and soil samples because of the differences in the formation and chemical composition of the rocks from which the ores were formed.[8, 9] Therefore, lead IR inherit the geological character of a production area. This factor has also been used for determining the geographic origin of wine[6, 10] and rice.[11]

Although thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) are highly precise (<0.005%) and are considered the best methods for measuring the lead IR, they are very expensive for regular use in most testing laboratories.[12–14] Quadrupole ICP-MS (Q-ICP-MS) instruments are less expensive, have higher sample throughput, and are used in many laboratories. However, this method shows less precisions (0.1–0.5%) compared to TIMS and MC-ICP-MS methods.[15–17] Bandura *et al.* reported that collisional damping by a non-reactive gas (Ar or Ne) in a reaction cell results in improved precision of IR (0.03–0.1%).[18]

This application note shows the capabilities of the PlasmaQuant MS Elite for the determination of lead isotope ratios in a variety of cigars coming from different regions to evaluate a potential discrimination based on their origin.

Materials and Methods

Instrumentation

The PlasmaQuant MS Elite Q-ICP-MS (Analytik Jena GmbH, Germany) was used in three different modes of conditions (He, No Gas, and H_2) for multi-element quantification, and in hydrogen operation mode for isotope ratios determination. This mode allows for the enhancement of sensitivity for high masses compared to the standard mode and a better precision for IR measurements without forming any hydride species. All experiments were carried out under standard environmental conditions at the Advanced Isotopic Analysis (AIA) Laboratory in Pau, France. The PlasmaQuant MS Elite operating conditions for isotope ratios measurements 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	0.00 L/min
Nebulizer gas flow	1.11 L/min
iCRC Gas Setting	H_2 – 0.03 L/min
Plasma RF power	1.40 kW
Dwell times	^{203}Tl – 3,000 µs ^{205}Tl – 2,000 µs ^{206}Pb – 3,000 µs ^{207}Pb – 3,000 µs ^{208}Pb – 2,000 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 except the first extraction and entrance lenses that were optimized manually to increase instrument sensitivity for high masses
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)
- Pb isotopic standard reference material SRM 981 (1 g wire of high-purity lead metal, NIST, USA)
- Tl isotopic standard reference material SRM 997 (0,25 g of high-purity thallium metal, NIST, USA)

Sample Preparation

Cigars are constituted of wrappers, binders, and fillers. These three parts can have a different origin and only the fillers are really originating of the producing country. Sample preparation for lead isotopic analysis consisted in a preliminary step of separating these parts followed by a digestion of the samples prior to analysis. The TOPwave (Analytik Jena GmbH) microwave digestion system (settings in Table 2) was used to digest 15 different types of cigars and 1 cigarette coming from different countries (Cuba, Nicaragua, Brazil, Dominican Republic, Peru, Honduras, Costa Rica, and Nicaragua). Some cigar samples were provided by Instituto de Investigaciones del Tabaco (Tabacuba, Cuba). After digestion, all samples displayed a clear transparent appearance and were ready for isotopic analysis.

To ensure quality control, several procedural blanks went through all steps of the same procedure and a certified reference material of tomato leaves (NIST SRM 1573a, USA), where Pb isotopes ratios have been already reported[19], was prepared with the same procedure.

Table 2: Digestion method parameters used on the TOPwave microwave digestion system

Parameter	Specification
Sample amount	0.5 g
HNO_3 volume	7 mL
H_2O_2 volume	3 mL
Vessel type	PM60
Heating stage 1 / ramp time	170 °C / 10 min
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

Major and Minor Elements Analysis

Calibration solutions were prepared from high-purity, multi-elemental standards (CCS-4 and CCS-6, Inorganic Ventures, U.S.) in 2% HNO_3 covering the following concentration ranges:

- 500–10,000 µg/L for Mg
- 100–2,000 µg/L for Al and Mn
- 50–1,000 µg/L for Sr
- 10–200 µg/L for Cu and Zn
- 5–100 µg/L for B
- 0.5–10 µg/L for Co, Ni, As, Rb, Cd, and Pb

Following digestion, all cigars' samples were transferred to 50 mL plastic containers and made up to volume with ultrapure water. Major and minor elements were measured by ICP-MS after a further 10-fold dilution in 2% HNO_3.

Lead Isotope Ratio Optimization

In terms of mass bias correction, several options were considered:

- Internal standard (using thallium, determination of the β factor)
- External standard: sample standard bracketing method (SSB)
- Double correction: internal and external standards

The operating parameters of the Q-ICP-MS were optimized daily using the thallium and lead standard solutions at a concentration of 0.5 and 5 µg L^{-1} respectively, to achieve the maximum sensitivity and stability for thallium and lead signals. The typical sensitivity for the isotope ^{205}Tl was 0.25 Mcps and 2.5 Mcps for ^{208}Pb at the concentrations mentioned previously. The injection of a low flow (0.03 L/min) of H_2 increased the sensitivity of the high masses and improved isotope precision.

It was noticed that the use of thallium as an internal standard degraded the precision. Some tests on different Pb/Tl ratios (1, 2, 3, 4, 5 and 10) showed that a ratio of 3 is optimal. However, the precision obtained with this ratio is still worse than a simple external correction. The best precision of 0.04% was achieved for both ratios, ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb, using a conventional Sample-Standard Bracketing (SSB) calibration sequence with the NIST SRM 981 as bracketing standard, combined with a blank correction.

Besides the mass bias correction, the effect of integration times (dwell times, number of scans and replicates) was investigated on the precision of the IR measurements, as follows. The goal was to obtain the best precision while keeping the shortest analysis time.

Evaluation of the Dwell Times, Scans and Replicates Ratio

To achieve the best precision, the optimum dwell times were evaluated using different times for the isotope ^{208}Pb. The dwell times for the other isotopes of Pb, ^{206}Pb and ^{207}Pb, were set using the following formula and are reported in table 3:

$$Dwell\ time(^{xxx}Pb\ ) = Dwell(^{208}Pb) \times \sqrt{\%(^{208}Pb)/\%(^{xxx}Pb)}$$

where %(^{xxx}Pb) and %(^{208}Pb) are the natural abundances of the lead isotopes. [20]

Table 3: Dwell time in µs for Tl and Pb isotopes and total estimated time of analysis using 400 scans and 30 replicates

Option	Dwell time [µs]					Total estimated time [s]
	^{203}Tl	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb	
1	750	500	750	750	500	483
2	1,500	1,000	1,500	1,500	1,000	522
3	3,000	2,000	3,000	3,000	2,000	600
4	7,000	5,000	7,000	7,000	5,000	816
5	15,000	10,000	15,000	15,000	10,000	1224

Figure 1a) and Figure 1b) show the precision, expressed as relative standard deviation (% RSD) of both IR measurements of a 5 µg/L lead isotopic standard solution (NIST 981) with increasing dwell times (Table 3).

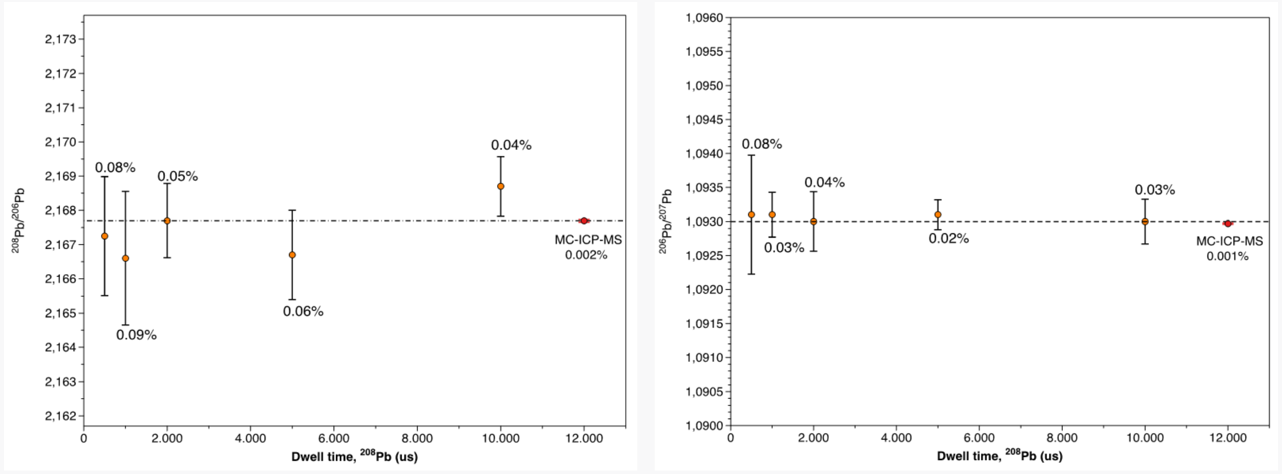


Figure 1a) %RSD of ^{208}Pb/^{206}Pb vs. ^{208}Pb dwell time
Figure 1b) %RSD of ^{206}Pb/^{207}Pb vs. ^{208}Pb dwell time for NIST SRM 981. Error bars are 1*SD

Following these tests, the dwell times for ^{208}Pb were set at 2,000 µs and therefore 3,000 µs for ^{206}Pb and ^{207}Pb. Using longer dwell times doesn't necessarily improve the precision and the accuracy of measurement in a significant manner and affects the total analysis time. However, such combination has a total estimated analysis time of 600 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	10	100	570
2	600	20	30	600
3	400	30	13	600
4	200	50	4	570
5	100	99	1	569

Figure 2a) and Figure 2b) show a good compromise of precision and total acquisition time using a scans/replicates ratio closer to 1 (less scans and more replicates), which delivers a precision of 0.02% for ^{208}Pb/^{206}Pb and 0.03% for ^{206}Pb/^{207}Pb in 10 minutes measuring time per sample.

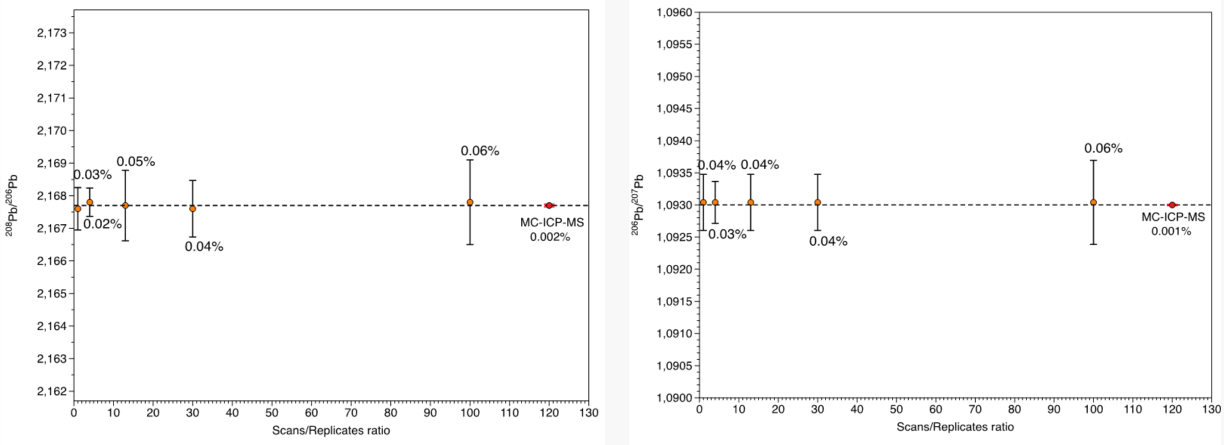


Figure 2a) %RSD of ^{208}Pb/^{206}Pb vs. Scans/Replicates ratio
Figure 2b) %RSD of ^{206}Pb/^{207}Pb vs. Scans/Replicates ratio for NIST SRM 981. Error bars are 1*SD

Results and Discussion

The multi-element composition of the 15 cigars and 1 cigarette are listed in table 5 and the lead isotopic ratios in table 6. More information about cigar's origin and results were presented in a poster during the *International congress of tobacco research*.[21]

Table 5: Major and minor elements concentrations in mg/kg for all samples measured by PlasmaQuant MS Elite and MC-ICP-MS

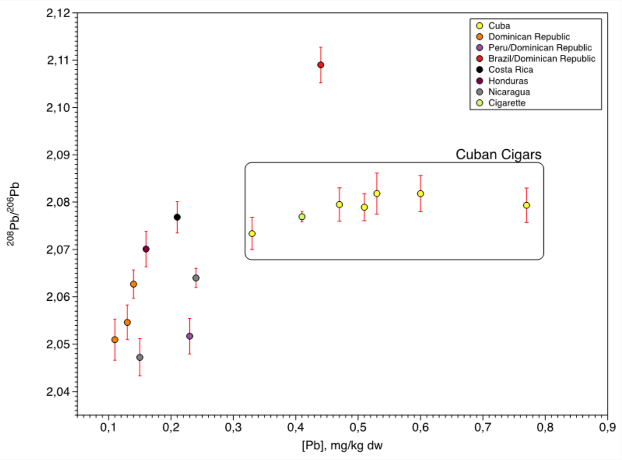
Sample ID	Origin	Concentration in mg/kg, dry weight												
		B	Mg	Al	Mn	Co	Ni	Cu	Zn	As	Rb	Sr	Cd	Pb
1_Cigar	Cuba	33	5,530	544	1505	1.9	4.5	26	128	0.14	13	119	3.4	0.33
2_Cigar	Cuba	36	4,773	960	209	0.28	0.63	5.0	42	0.20	8.7	103	1.3	0.77
3_Cigar	Cuba	36	8,469	789	219	0.50	2.8	13	61	0.16	8.9	136	2.2	0.47
4_Cigar	Cuba	35	9,965	828	211	0.47	4.0	11	54	0.16	8.6	147	2.3	0.51
5_Cigar	Nicaragua	55	7,555	856	255	0.44	1.5	8.5	31	0.27	7.5	179	0.67	0.15
6_Cigar	Brazil/Dom. Republic	47	10,755	1223	108	0.52	3.3	165	80	0.27	17	201	0.46	0.44
7_Cigar	Peru/Dom. Republic	38	7,459	805	238	0.61	2.3	14	64	0.18	9.2	416	0.45	0.23
8_Cigar	Dom. Republic	39	5,064	708	353	0.42	1.06	21	132	0.07	2.8	225	0.80	0.11
9_Cigar	Cuba	23	5,733	918	497	0.32	1.3	8.7	66	0.14	9.3	80	2.3	0.60
10_Cigar	Dom. Republic	35	8,553	851	335	0.49	2.2	27	67	0.09	6.5	215	0.70	0.14
11_Cigar	Honduras	44	8,566	732	148	0.61	3.3	31	81	0.65	10.2	169	2.8	0.16
12_Cigar	Cuba	26	6,968	608	272	0.46	2.6	8.7	74	0.18	16	100	3.4	0.53
13_Cigarette	Unknown	33	4,866	887	181	0.73	2.9	12	37	0.13	28	118	0.71	0.41
14_Cigar	Dom. Republic	53	8,009	771	126	0.52	3.5	24	57	0.12	5.9	502	0.36	0.13
15_Cigar	Costa Rica	33	5,652	678	253	0.27	0.95	8.8	73	0.07	6.4	156	0.87	0.21
16_Cigar	Nicaragua	36	7,647	1375	292	0.70	2.3	13	98	0.19	15	138	2.0	0.24

A wide range of toxic metals can be deposited on tobacco leaves from particles in the air and some fungicides and pesticides have been sprayed on tobacco leaves or soils in the past. However, most of the metals present in plants are absorbed from the soil depending on where the tobacco has grown. Table 5 clearly shows that elements such as magnesium, aluminum, manganese, copper, zinc, and strontium are considered as the major ones. Lower concentrations of arsenic, cadmium, and lead were also found and could potentially come from the use of fertilizers, even though the soil where the tobacco has grown and the air quality, especially for lead in polluted/industrial areas, also plays a major role. According to table 5, cadmium and lead seem to provide already a good indication on samples origin because of the differences of concentrations of the samples originating from Cuba and the other ones.

Table 6: Isotope ratios of lead, $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$, standard deviations and %RSD measured by the PlasmaQuant MS Elite

Sample ID	Origin	$^{208}Pb/^{206}Pb$	SD	%RSD	$^{206}Pb/^{207}Pb$	SD	%RSD
1_Cigar	Cuba	2.073	0.003	0.16	1.182	0.002	0.15
2_Cigar	Cuba	2.079	0.004	0.18	1.180	0.002	0.17
3_Cigar	Cuba	2.079	0.004	0.17	1.179	0.001	0.08
4_Cigar	Cuba	2.079	0.003	0.14	1.179	0.001	0.11
5_Cigar	Nicaragua	2.047	0.004	0.19	1.197	0.002	0.17
6_Cigar	Brazil/Dom. Republic	2.109	0.004	0.18	1.161	0.002	0.17
7_Cigar	Peru/Dom. Republic	2.052	0.004	0.18	1.201	0.002	0.18
8_Cigar	Dom. Republic	2.051	0.004	0.21	1.193	0.002	0.18
9_Cigar	Cuba	2.082	0.004	0.18	1.178	0.002	0.18
10_Cigar	Dom. Republic	2.063	0.003	0.15	1.190	0.002	0.15
11_Cigar	Honduras	2.070	0.004	0.18	1.194	0.002	0.16
12_Cigar	Cuba	2.082	0.004	0.21	1.177	0.002	0.18
13_Cigarette	Unknown	2.077	0.001	0.05	1.189	0.001	0.08
14_Cigar	Dom. Republic	2.055	0.004	0.18	1.194	0.002	0.15
15_Cigar	Costa Rica	2.077	0.003	0.16	1.181	0.002	0.16
16_Cigar	Nicaragua	2.064	0.002	0.10	1.192	0.002	0.13

In terms of isotope ratios, Table 6, Figure 3 and 4 reveal that lead, but also cadmium can provide an excellent indication on the origin of the samples. There is a clear discrimination between Cuban cigars and other ones using lead isotopes versus lead or cadmium concentration.



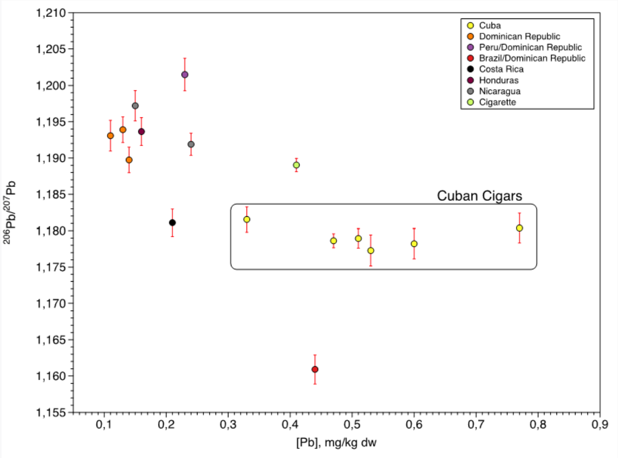


Figure 3a) $^{208}Pb/^{206}Pb$ vs. [Pb]
Figure 3b) $^{206}Pb/^{207}Pb$ vs. [Pb] for all the samples measured by PlasmaQuant MS Elite

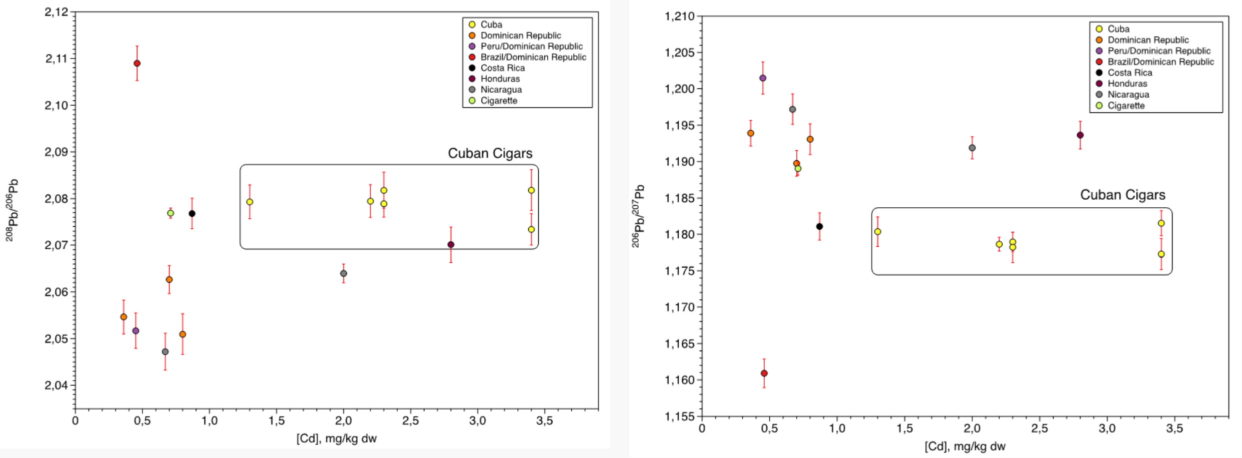


Figure 4a) ^{208}Pb/^{206}Pb vs. [Cd]
Figure 4b) ^{206}Pb/^{207}Pb vs. [Cd] for all the samples measured by PlasmaQuant MS Elite

The analyses of NIST 981 also provided a record of the stability of the measurements and the final mass bias over the course of the experiments. The values of the SRM 981 IR for a series of analyses over a period of 22 hours are shown in Figure 5. Table 7 lists the means and confidence levels ($p = 0.05$) of 21 measurements of the two ratios, along with the certified values, which shows a very minor deviation, ranging from -0.002% for ^{208}Pb/^{206}Pb to 0.001% for ^{206}Pb/^{207}Pb only.
The long-term stability of PlasmaQuant MS Elite, using the optimized conditions was excellent. The ratios ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb precisions were 0.05% and 0.06%, respectively.
Additionally, one of the cigar samples was prepared and analyzed three times separately. The method precision obtained using the PlasmaQuant MS Elite was 0.09%, which considered not only the measurement step but also the preparation.

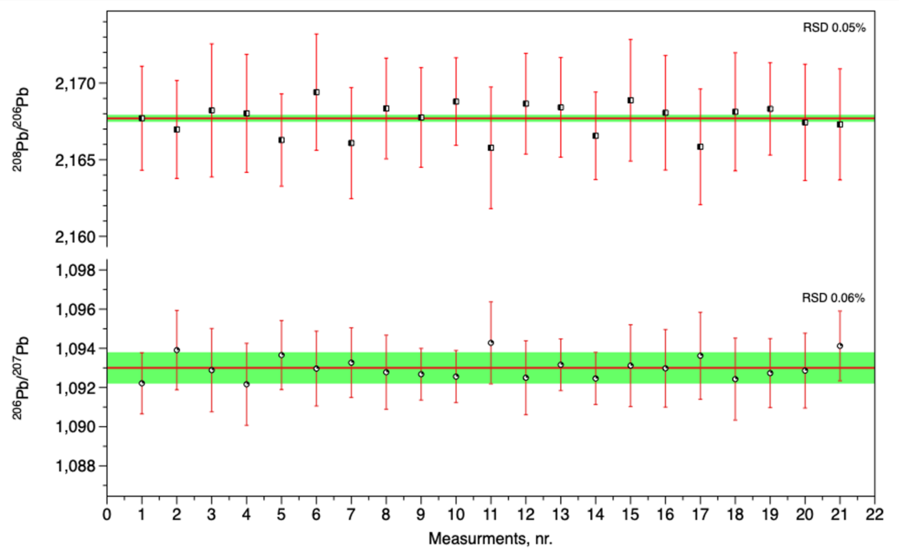


Figure 5: NIST 981 stability over 22 hours of total measurements using the standard bracketing approach. The solid lines and the green interval represent the Thirlwall[22] obtained values using double spike method and 2SD of both IR. The mean RSDs of all the 21 measurements are also shown.

Table 7: NIST 981 IR measurements vs. values obtained by Thirlwall obtained by double spike method. Values and 2SD of both IR

Ratio	Measured	Thirlwall	Difference [%]
$^{208}Pb/^{206}Pb$	2.1676 ± 0.0010	2.1677 ± 0.00023	-0.002
$^{206}Pb/^{207}Pb$	1.0930 ± 0.0006	1.0930 ± 0.0008	0.001

Conclusion

A method was developed for the digestion and subsequent lead isotope ratios measurements of cigar samples via Q-ICP-MS. The method required minimal sample preparation and allowed rapid analysis times. The precision of the lead isotope ratios in PlasmaQuant MS Elite was less than 0.02 % for the $^{208}Pb/^{206}Pb$ and less than 0.03% for the $^{206}Pb/^{207}Pb$ ratios.
Due to the excellent precision achieved by the PlasmaQuant MS Elite, it was possible to distinguish the Cuban cigar samples from others grown in different geographic regions. The very high sensitivity of the instrument allowed to use short dwell times; therefore, the measurements were carried out in a fast manner without compromising the precision.

However, to use such promising technique as a forensic tool to determine the origin of tobaccos, many cigarette/cigar samples from different tobacco producing regions would have to be analyzed to generate a useful geographic database of lead isotope ratios. This database would probably need to be updated periodically due to changes in the lead isotope ratios from atmospheric deposition and other processes.

The use of a high resolution (single or multiple ion detector magnetic sector) ICP-MS spectrometer and/or combining IR of lead with IR of other elements (e.g., Sr, B) might also improve the ability to determine the geographic origin of different tobacco products.

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