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Classification of the geographic origin of cigarettes according to Pb isotope ratios by inductively coupled plasma dynamic reaction cell mass spectrometry

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Abstract

Trace Pb is accumulated in the same isotopic ratio as it occurs in the source soil, and the isotopic composition of Pb could be used to reflect these sources and provide powerful indicators of the geographic origin of agricultural products. In this study, we developed a simple and valid method based on inductively coupled plasma dynamic reaction cell mass spectrometry (ICP-DRC-MS) for the determination of Pb isotope ratios to distinguish between the geographic origins of cigarettes. The cigarette digestion solutions were directly analysed by ICP-DRC-MS with pressuring a non-reactive gas Ne. In the DRC, Ne molecules collide with Pb ions and result in a 2.3-fold improvement in the average internal precision of Pb isotope ratios, which may be due to the improvement of the ion transmission or sensitivity (via collisional focusing) and the reduction of the plasma noise (via collisional energy dampling). Under the optimum DRC rejection parameter Q (RPq = 0.45), the main matrix components (K, Na, Ca, Mg, Al, Fe, *etc.*) originating from cigarettes were filtered out. Other important parameters such as detector dead time, dwell time per data acquisition and total integrated time per isotope were also optimized. Mass discrimination of $^{208}Pb/^{206}Pb$ ratio in Ne DRC mode increased to 0.3% compared to the vented mode, this mass bias could be accurately corrected by using the NIST 981 Pb isotope standard solution. The accuracy and precision of this method were evaluated by using two cigarette reference materials (Oriental tobacco leaves CTA-OTL-1 and Virginia tobacco leaves CTA-VTL-2). Results of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ were 2.0842 ±0.0028 (2δ) and 0.8452 ±0.0011 (2δ) for CTA-VTL-2, which were in agreement with the literature values ($^{208}Pb/^{206}Pb$ = 2.0884±0.0090 and $^{207}Pb/^{206}Pb$ = 0.8442±0.0032), respectively. The Pb isotopic composition ($^{208}Pb/^{206}Pb$ = 2.0812±0.0028 and $^{207}Pb/^{206}Pb$ = 0.8460±0.0018) of CTA-VTL-1 was reported for the first time in our study. The precision of Pb isotope ratios ($^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$) for the

cigarette samples ranged from 0.05 to 0.12 % (N = 6). The proposed method has sufficient precision to distinguish between 91 cigarette brands originated from four different geographic regions.

Introduction

Although cigarette smoking kills approximately 6 million people worldwide and causes more than 5000 billion dollars of economic damage each year [1], the number of daily smokers increased from 721 million in 1980 to 967 million in 2012 [2]. Cigarettes accounted for 80 %of the global tobacco production of 5.2 million tons per year. The globalization of tobacco markets resulted in easy tobacco trade between countries; however, the consumers are increasingly concerned about the origin of their cigarettes. Therefore, rapid and valid profiling techniques should be established to identify the geographic origin of cigarettes.

Plants accumulate trace metals from the soil and they are deposited on the foliage. Since the elements are accumulated in the same isotopic ratios as they occur in the source soil, the isotopic ratio reflects the sources and indicates the geographic origin of products derived from vegetative matter[3]. The following two techniques based on isotopic ratio have been used to determine the geographic origin of agricultural products: 1) isotope composition of light elements (H, B, C, N, O, S, *etc.*) and 2) ratios of heavy elements (Sr, Pb, *etc.*) [4-11]. Compared to light elements, isotopes of heavy elements are rarely fractionated in the terrestrial ecosystem, and the latter are more advantageous for determining geographic origin [12]. In general, there is no difference in the isotope ratio between a crop and its exchangeable fraction in the soil as long as the crop is grown under the same soil and water conditions. Establishing the isotope ratio database of a product

helps to identify whether other new products belong to this category. The major fraction of Pb 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 Pb is of particular interest because ^{208}Pb, ^{207}Pb and^{206}Pb are derived from the radioactive decay of ^{232}Th, ^{235}U and ^{238}U, respectively [13]. Large variations in Pb isotopic ratios (0.82–0.95 for ^{207}Pb/^{206}Pb, and 2.02–2.22 for ^{208}Pb/^{206}Pb) 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 [14,15]. Therefore, Pb isotope ratios inherit the geological character of a production area and this factor has been used for determining the geographic origin of wine [15-17] and rice [18].

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 to be the best methods for measuring the Pb isotope ratios, they are very expensive for regular use in most of the testing laboratories [19-24]. Quadrupole ICP-MS (ICP-QMS) instruments are less expensive, higher sample throughput and are used in many laboratories. However, this method is less poor precision (0.1–0.5%) compared to the TIMS and MC-ICP-MS methods [25-29]. Recently, Bandura *et al.* reported that collisional damping by a non-reactive gas (Ar or Ne) in a dynamic reaction cell (DRC) results in improved precision of isotope ratios (0.03~0.1%) [30]. It had been demonstrated that the collisions with the non-reactive gas molecules increase the average residence time of the analyte ions in the cell and that ions sampled at slightly different moments in time are actually mixed [30]. As a consequence, short-term fluctuations of the ion signal intensities are damped and the precision of the isotope ratios are improved [30-33]. This method had been used for measuring the Pb isotope ratios in the atmosphere [31], archaeological artefacts [32], snow and sediment [34]. However, the mass discrimination due to in-

cell fractionation effects also existed in these complex samples and a chromatographic extraction step was required to separate Pb from the concomitant matrix [31-33]. Fortunately, the main concomitant matrix (K, Na, Ca, Mg, Fe, Sr, Ba, *etc*.) of tobacco samples are less complex than the soil or rock matrices; hence, mass discrimination due to matrix elements in the DRC may be alleviated without subsequent isolation processes. The total Pb concentration of cigarettes in various regions typically ranged from 0.5–6.5 μg/g [35-38], which are sufficiently high concentrations for measuring isotope ratios by ICP-QMS.

In this study, we present an analytical procedure for the determination of Pb isotope ratios in cigarettes for classifying their geographic origin. We optimized the technique, its analytical performance, as well as its application to the determination of Pb isotope ratios in 91 different brands of cigarettes procured from seven countries. Differences in the Pb isotope ratios allowed the evaluation of the proposed method as a potential tool for tracing cigarette provenance.

Experimental

Instrumentation

A PerkinElmer SCIEX ELAN DRC-e ICP-MS instrument was used. A PFA-400 MicroFlow (self-absorption, 0.1 mL min^{-1}) nebulizer interfaced with a cyclonic spray chamber (PC^3 Peltier Chiller) was used with a 2.0 mm i.d quartz injector tube, which is described in detail elsewhere [39,40]. The operating parameters of the DRC-ICP-MS are summarized in Table 1. Under the optimized operating conditions, the sensitivity of ^{208}Pb was >15,000 cps/ng mL^{-1}. High purity Ar and Ne gases (99.999% purity) for ICP-MS were purchased from Praxair Investment Co., Ltd, China.

Reagents and standards

High purity water (18.2 MΩ cm^{-1}) used for the preparation of all standards, blanks and sample solutions was produced by a Millipore water purification system (Millipore, France). Nitric acid (HNO_3, 99.9999%), hydrofluoric acid (HF, 99.999%) and hydrogen peroxide (H_2O_2, 99.999%) were purchased from Alfa Aesar Ltd. (Tianjin). The Pb isotopic standard (1000 mg L^{-1}) was prepared by dissolving 1 g of NIST SRM 981 in HNO_3 (Merck, Germany). Working standard solutions were prepared daily by diluting the stock solution in 1% (v/v) HNO_3.The accuracy and precision of the method were evaluated by using two cigarette reference materials (RMs), namely oriental tobacco leaves (CTA-OTL-1) and Virginia tobacco leaves (CTA-VTL-2), obtained from the Institute of nuclear chemistry and technology (INCT), Warsaw, Poland. The total Pb concentration of CTA-OTL-1 and CTA-VTL-2 were 4.88 ± 0.14 μg $g^{-1}$and 22.1 ± 0.4 μg g^{-1}, which were in good agreement with the certified valuesof 4.91 ± 0.80 μg $g^{-1}$and 22.1 ± 1.2 μg g^{-1}, respectively.

Sampling and sample preparation

Seventy tobacco samples of various Chinese brands were purchased from 21 tobacco shops of the China national tobacco corporation (CNTC). Other tobacco samples were purchased from the overseas markets. Five brands (CAMEL-1, CAMEL-2, SHAMAN'S, MARLBORO-1 and MARLBORO-2) were obtained from the United States, three brands (EXPORT, du MAURIER and L&M) from Canada, three brands (TREASURER, KENT and LAMBERT & BUTLER) from England, three brands (BLACK, ARDATH and BENTOEL) from Indonesia, two brands (BACSON and AROMA) from Vietnam and five brands (TIME, ESSE LIGHTS,RAISON,ESSE and TONINO LAMBORGHINI) from Korea. All the samples were stored in plastic bags and

refrigerated (4°C). The samples were oven-dried at 60°C and manually ground by using an agate mortar to obtain the desired particle size (≤75μm). Following which, 250 mg of the powdered sample was placed in a 25 mL home-made PTFE-lined stainless steel bomb. 3 mL of $HNO_3$and 0.5 mL of HF were added to the bomb and heated at 120 °C to dryness (but not baked) on a hot plate. After cooling, 3 mL of $HNO_3$and 2 mL of H_2O_2 were added and the bomb was sealed and placed in an electric oven and heated to 180 °C for 6 h. After cooling, the bomb was opened and placed on a hot plate (at 120 °C), and evaporated to incipient dryness. Then, 1.0 mL of HNO_3 and 2.0 mL of ultra-pure water were added and the bomb was covered and gently heated to extract Pb from the residues. The final solution was made up to 25 mL by adding ultra-pure water. For the high Pb concentration (22.1 ± 1.2 μg g^{-1}) of the CTA-VTL-2 RM, the dilution factor was 1000-fold.

Results and discussion

Collisional focusing for the precise measurement of Pb isotope ratios

Application of ICP-QMS has been advantageous for measuring Pb isotope ratios because of the high sample throughput, ease of sample preparation and low cost of analysis compared toother techniques. However, poor precision ranging from 0.1–0.5% RSD ($^{208}Pb/^{206}Pb$ or $^{208}Pb/^{207}Pb$) may be obtained with the traditional ICP-QMS (without reaction or collision cell) [41,42], thus making it difficult to distinguish between the Pb sources from different geographical origins; therefore, efforts should be made to improve precision. In this study, Ne, a non-reactive gas,was studied as a DRC collision gas for improving the precision of Pb isotope ratios. Fig. 1a shows the effect of increasing Ne flow on the average internal precision (ratio RSD of 5 replicates was

measured 6 times and then the average of 6 RSDs taken) of $^{208}Pb/^{207}Pb$ for 10 ng mL^{-1} of the NIST 981 standard solution. As shown in Fig. 1a, the advantage in terms of precision is significant, the precision improved 2.3-fold by the pressurized DRC mode (Ne = 0.3 mL min^{-1}) compared to the DRC vented mode (Ne = 0), which is similar to the values (~2.5 fold) reported by Bandura *et al.*[30] and Resano *et al.*[41] The ratio RSD (average internal precision) for he pressurized cell (Ne = 0.3 mL min^{-1}) is 0.072% with a corresponding counting statistics error (SE) of 0.069%, whereas for the vented mode (Ne = 0) it is 0.17% and 2.5 times higher than the counting SE (Fig. 1a). Fig. 1b shows the effects of the average internal precision and the counting SE as a function of the total counts of ^{208}Pb and ^{206}Pb, the average internal precision follows closely the counting SE at the selected range. On the other hand, the signal intensities of ^{208}Pb and ^{206}Pb were enhanced by up to 3 times with pressurized cell (Ne = 0.3 mL min^{-1}), which is due to the improvement of the ion transmission (via collisional focusing) (Fig. 1c). A high counts could be beneficial for obtaining the high precision isotope ratios, but the sensitivity improvement could only improve 1.7-fold (square root of 3) for the precision, as a result, there may be other factors affect the precision. Bandura et al. [30] demonstrated that short-term ion signal fluctuations are damped by the collisions with a high Ne gas flow (1.5-2.0 mL min^{-1}), and the precision of isotope ratios are improved. To avoid large mass discrimination (Fig. 4) and collisional scattering, a low Ne gas flow (0.30 mL min^{-1}) was selected in our study. Therefore, we speculate that the ion transmission or sensitivity improved by collisional focusing, in combination with the reducing plasma noise by collisional energy dampling, results in a better precision. Another important parameter is the rejection parameter Q (RPq) of DRC. In this study, the optimum RPq value of 0.45 (Table 1) provided the best transmission efficiency in the DRC when operated in the pressurized mode. Meanwhile, an RPq value of 0.45 for an m/z of 206

results in a cut-off at approximately m/z = 102 [41], resulting in the filtering out of the main matrix components (K, Na, Ca, Mg, Al, Fe, *etc.*) of the cigarettes. Therefore, a combination of high sensitivity, low matrix effect and improved plasma noise with collisional damping result in an improved precision of Pb isotope ratios.

Optimization of the data acquisition parameters

Data acquisition parameters such as detector dead time, dwell time per data acquisition and total measurement time per isotope should be optimized to obtain best precision while measuring isotope ratios by ICP-QMS. The dead time associated with detector response leads to counting losses that increase in magnitude with increasing counting rate [43]. This leads to inconsistencies in the isotope abundance ratio measurements that are independent of mass discrimination effects; therefore, the inconsistencies must be corrected prior to correcting mass discrimination. The detector dead time was determined according to a method proposed by Nelm *et al*.[44]. The results of the $^{206}Pb/^{208}Pb$ isotope ratio measurements versus dead time applied in the software are presented in the ICP-DRC-MS data shown in Fig. 2. Dead time was determined from the dead times corresponding to each intersection point and a value of 53 ns was obtained from calculations (Fig. 2). The obtained value was in agreement with the manufacturer's recommended value (55 ns for DRC-e ICP-MS) and it was similar to the reported values (61 ns for DRC $_{plus}$ ICP-MS) [41]. As shown in Fig. 3a, the best precision (0.03–0.05% for $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$) was obtained at dwell time values of 1, 2 and 2ms for ^{208}Pb, ^{206}Pb and ^{207}Pb, respectively. The optimum total measurement time per replicate was also evaluated by changing the number of sweeps and/or readings from 1 to 1000. When the value was higher than 59 s per replicate measurement, no improvement in precision was observed as shown in Fig. 3b.In

addition, the optimum replicate was selected as five times because precision remained constant from 5 to 11 times of replication. The total measurement time was 5 min 46 s per sample. Other optimized parameters are listed in Table 1.

Mass bias correction and analytical performance

Mass discrimination effects should also be corrected for accurate isotope ratio determination. Mass discrimination is the bias between the experimental value (after correcting detector dead time and procedure blank) and the corresponding 'true' value. Some studies [45,46] reported that the collision gas in the collision/reaction cell affects mass discrimination. Xie *et al.*[45] reported that for a quadrupole-based instrument equipped with a radio frequency (rf) only hexapole collision cell, the use of He and H_2 does not affect mass discrimination. However, Boulyga and Becker reported that the use of He resulted in the collisional focusing of heavier ions, while the lighter ions suffered from collisional scattering, leading to mass discrimination.[46] Therefore, it is important to investigate the mass discrimination of Ne in DRC for the determination of Pb isotope ratios in tobacco samples. In our preliminary experiments, a digested solution (20 ng mL^{-1}) of CTA-VTL-2 was used to study the effect of Ne gas flow rate on the $^{208}Pb/^{206}Pb$ isotope ratios. As shown in Fig. 4, Pb isotope ratios increased with increasing Ne flow rate. At the optimum Ne gas flow rate of 0.3 mL min^{-1}, the $^{208}Pb/^{206}Pb$ ratio increased by 0.3% (from 2.0848 to 2.0911) compared to the standard mode (DRC vented). Mass bias due to the in-cell Ne gas collision can be accurately corrected because both the cigarette samples and isotopic standards are measured under the same conditions. The measurement sequence consisted of 1% HNO_3 blank, 20 ng mL^{-1} NIST SRM 981 Pb standard solution, produce blank, sample 1, NIST 981 standard, sample 2, NIST 981 standard and so on. The obtained Pb isotope ratios were corrected

for mass discrimination by the external bracketing technique and the true sample ratios ($R_{true,\ sample}$) were calculated as follow:

$$R_{\mathrm{true,sample}} = R_{\mathrm{NIST,cert}} * \frac{R_{\mathrm{detect,sample}}}{\frac{R_{\mathrm{NIST,before}} + R_{\mathrm{NIST,after}}}{2}}$$

where $R_{NIST,\ cert}$ is the certified value of NIST SRM 981 common Pb given by NIST. $R_{detect,\ sample}$ is the value after the blank correction procedure. After the above correction, the Pb isotope ratio was 2.0848±0.0028 for $^{208}Pb/^{206}Pb$, which is consistent with that of the vented mode (2.0849±0.0063). Two cigarettes RMs (CTA-OTL-1 and CTA-VTL-2) were used to evaluate the accuracy of the proposed method and their Pb isotope ratios are summarized in Table 2. For the CTA-VTL-2 RMs, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ were 2.0848 ± 0.0028 and 0.8452 ± 0.0011(2δ), respectively. Reproducibility ranged from 0.046–0.076% (N = 27) for the CTV-VTL-2 RM (Fig. 5) and a little upward trend of $^{208}Pb/^{206}Pb$ did not influence precision. Since the Pb isotope ratio values were not certified in both the RMs, the accuracy of the Pb isotope ratio measurements in the tobacco RMs were assessed by literature values. The detected values were in agreement with the values reported by Judd *et al.*[35], but the precision obtained in this study was obviously better than the reported values (Table 2). Pb isotopic composition is not yet published for the CTA-OTL-1 RM, for which our detected values were $^{208}Pb/^{206}Pb$ = 2.0812±0.0028 and $^{208}Pb/^{206}Pb$ = 0.8460±0.0018 (2δ) (Table 2). To confirm the value, ten separate aliquots of CTA-OTL-1 were digested and analysed in a period of three months. These analyses yielded Pb isotope ratio values ranging from 2.0809–2.0814 (average of 2.0812±0.0029) for $^{208}Pb/^{206}Pb$ and 0.8457 to 0.8463 (average of 0.8461±0.0016) for $^{208}Pb/^{206}Pb$, respectively. These values are in agreement with the above values (Table 2).

Classification of the geographic origin of cigarettes

A total of 91brands of cigarette samples from seven different countries were analysed by using the proposed method. When the dilution factor was fixed at 100-fold, the total Pb concentrations ranged from 7–49 ng mL^{-1}. Since the accuracy and precision values of Pb isotope ratios did not vary at Pb concentrations ranging from 5–80 ng mL^{-1} (Fig. 6), the digested solutions of the cigarette samples were directly measured by this method. Various brands fall into four distinct categories based on the $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios as shown graphically in Fig. 7. Each point represents one sample and the error bars are twice the standard deviation of each measurement (2δ).The average internal precision (N = 6) of Pb isotope ratios ($^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$) ranged from 0.05–0.12% for the cigarette samples. The $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios are statistically different at the $p = 0.05$ level or better between each group: the $^{208}Pb/^{206}Pb$ values of three cigarette brands originated from England (2.1295–2.1378) are higher than that of the other groups (2.0528–2.1180), and the $^{207}Pb/^{206}Pb$ values of cigarettes originated from Indonesia (0.8621–0.8656) are higher than that of the other three groups (0.8366–0.8580). The $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios of the cigarettes originated from North America (0.8353–0.8431 and 2.0528–2.0818) are lower than that of the other three groups (0.8456–0.8656 and 2.0813–2.1180). The Pb isotope ratios of cigarettes originated from East Asia (China, Korea and Vietnam) fall within the middle of the plot (Fig. 7). Interestingly, the $^{208}Pb/^{206}Pb$ ratio of one Chinese brand (Liqun) was high at 2.22 as reported by Judd *et al.*[35]; however, the $^{208}Pb/^{206}Pb$ ratios of cigarettes from 70 Chinese brands ranged from 2.08–2.13 (Fig. 7). This difference (>5%) is far beyond the measured precision. To explain this phenomenon, 16 Liqun cigarette samples (five kinds) collected from eight tobacco shops of CNTC were measured and the $^{208}Pb/^{206}Pb$ ratios ranged between 2.09 and 2.11 (Table S1 of the ESI.[†]), which fall within the range of 2.08–2.13. The difference of $^{208}Pb/^{206}Pb$ ratios occurred may be due to the only one

Liqun brand sample was analysed in Judd's paper [35], and was collected from the general store (not collected from the manufacturer of CNTC). Since the cigarettes originated from China, Korea and Vietnam have similar Pb isotope ratios, these different cigarette brands cannot be discriminated, which as well as the cigarettes from USA and Canada.

Conclusions

The proposed technique is simple, valid and has sufficient precision to distinguish between the different cigarettes brands originated from four different geographic regions. Further research is necessary to measure large number of cigarette samples produced from different regions and to generate a complete geographic database of Pb isotope ratios for classifying the geographic origin and to distinguish counterfeit cigarettes from legal samples.

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Figure captions

Fig.1 (a) Average RSD (%) for the $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios (N = 6, replicate = 5) as a function of the Ne collision gas flow rate, dotted lines show counting statistics error SE; (b) $^{208}Pb/^{206}Pb$ average internal precision for the pressurized with Ne at 0.3 mL min^{-1} cell and its corresponding counting SE as a function of the total accumulated counts; (c) Pb signal intensities as a function of the Ne collision gas flow rate.

Fig.2 $^{206}Pb/^{208}Pb$ ratio *versus* dead time.

Fig.3 Optimization of the dwell time per acquisition point (a) and the total measurement time per replicate (b) for Pb isotopic ratios in 20 ng mL^{-1} NIST SRM 981 Pb solution by ICP-DRC-MS with 0.3 mL min^{-1} Ne as the collision gas.

Fig.4 Effects of the Ne collision gas flow rate in DRC on the $^{208}Pb/^{206}Pb$ ratios in a digested solution (20 ng mL^{-1}) of the CTA-VTL-2 Virginia Tobacco Leaves.

Fig.5 Results of repeated analyses of a 20 ng mL^{-1} tobacco SRM CTA-VTL-2 solution. Average values of the NIST 981 corrected Pb isotope ratios are: $^{208}Pb/^{206}Pb$ = 2.0842 ± 0.0009 and $^{207}Pb/^{206}Pb$ = 0.8452 ± 0.0015 (2δ). The measured time is twenty-seven (N = 27).

Fig.6 Effects of the total Pb concentrations in the analyzed solution on the values of the accuracy and precision Pb ratios. Pb concentrations were ranged from 5 to 80 ng mL^{-1} of the NIST SRM 981 Pb solution.

Fig.7 Results for lead isotope ratios in 91 different brands of cigarette originated from seven different countries, plot of $^{208}Pb/^{206}Pb$ against $^{207}Pb/^{206}Pb$.

Tables

Table 1 Instrument operating parameters

ICP-MS instrument	Perkin-Elmer Sciex Elan DRC-e
Sample introduction	PFA-400 MicroFlow nebulizer (self sample absorption)
Spray chamber	Cyclonic spray chamber (PC^3 Peltier Chiller)
Injector tube	2.0 mm id Quartz
Interface cones	Ni, 1.1 mm i.d. for sampling cone, and 0.9 mm i.d. for skimmer cone.
RF power, W	1100
Plasma gas flow, L min^{-1}	15
Auxiliary gas flow, L min^{-1}	1.00
Nebulizer gas flow, L min^{-1}	0.85
Lens Voltage, V	8.0
Autolens	Off
DRC parameters	
Cell gas Ne, mL min^{-1}	0.30
Rejection parameter, q	0.45
Rejection parameter, a	0
QRO	-6
CRO	-1
CPV	-15
Data acquisition parameters	
Scanning mode	Peak hopping
Detector mode	Pulse counting
Detector dead time	53 ns
Dwell time	2 ms for $^{206}Pb^+$ and $^{207}Pb^+$, 1 ms for $^{208}Pb^+$

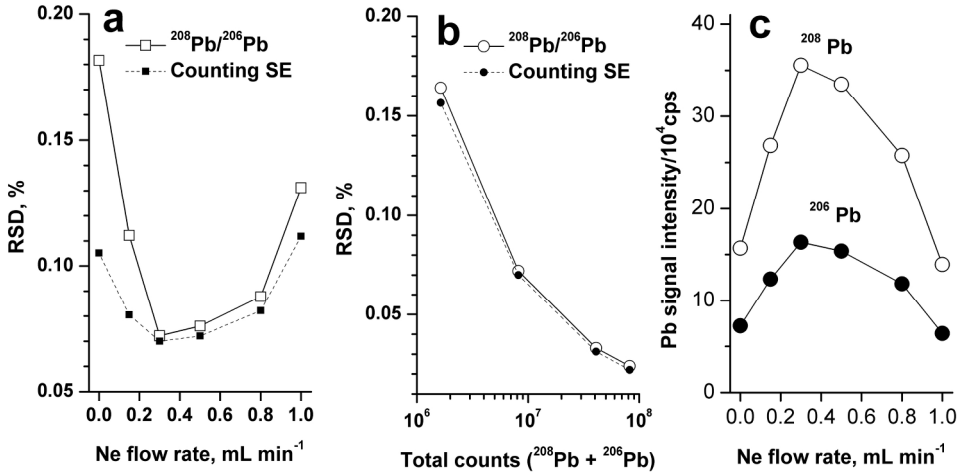
Settling time	200 µs
Sweeps	600
Readings	20
Replicate	5
Total measurement time	5 min 46 s per sample

Table 2 Pb isotope ratios of the two tobacco standard reference materials (CTA-VTL-2 and CTA-OTL-1) by this method

		This work		Reference ratios (2δ), Judd et al. (2010)
		Measured ratios (2δ)	Average internal precision (N =5), % [a]	
CTA-VTL-2	$^{208}Pb/^{206}Pb$	2.0842±0.0028	0.051	2.0884±0.0090
	$^{207}Pb/^{206}Pb$	0.8452±0.0011	0.072	0.8442±0.0032
CTA-OTL-1	$^{208}Pb/^{206}Pb$	2.0812±0.0028	0.049	/ [b]
	$^{207}Pb/^{206}Pb$	0.8460±0.0018	0.068	/

[a] Ratio RSD of 5 replicates was measured 6 times, then the average of 7 RSDs taken

[b] Non certified and literature reported value



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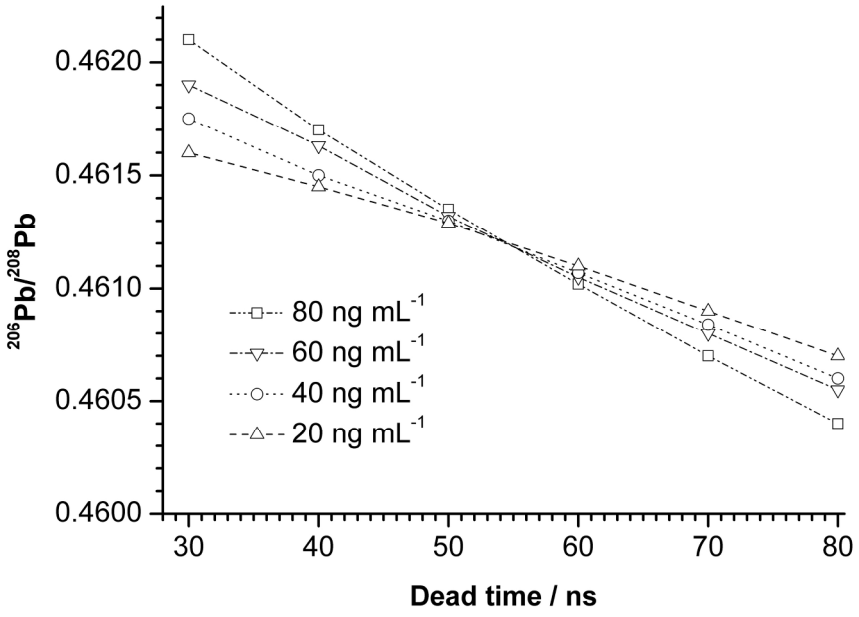
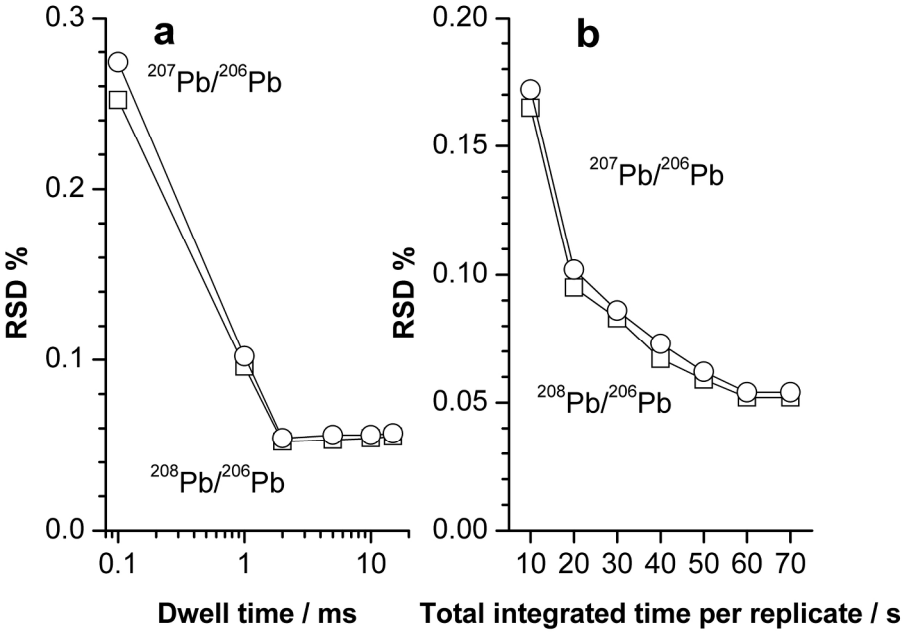


Fig.2 ^{206}Pb/^{208}Pb ratio versus dead time.
210x148mm (300 x 300 DPI)



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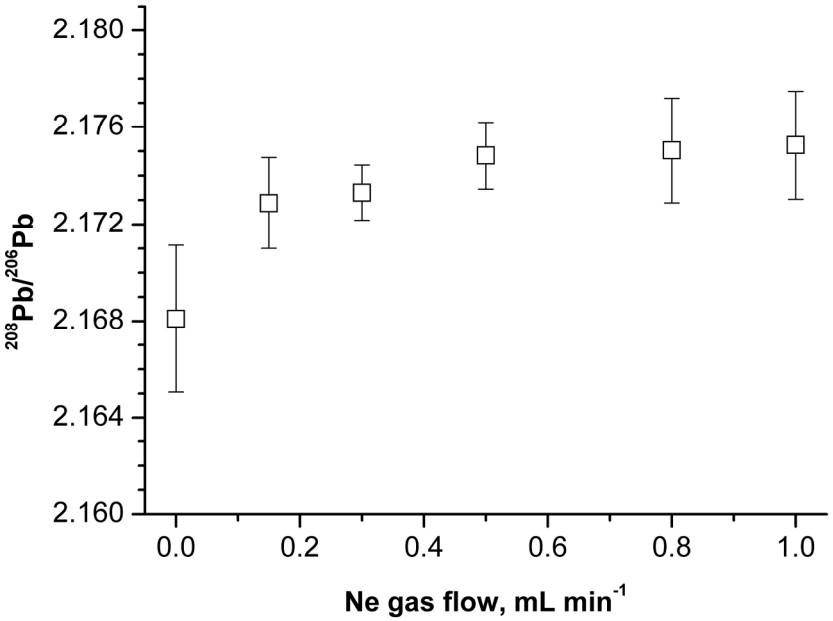
210x148mm (300 x 300 DPI)



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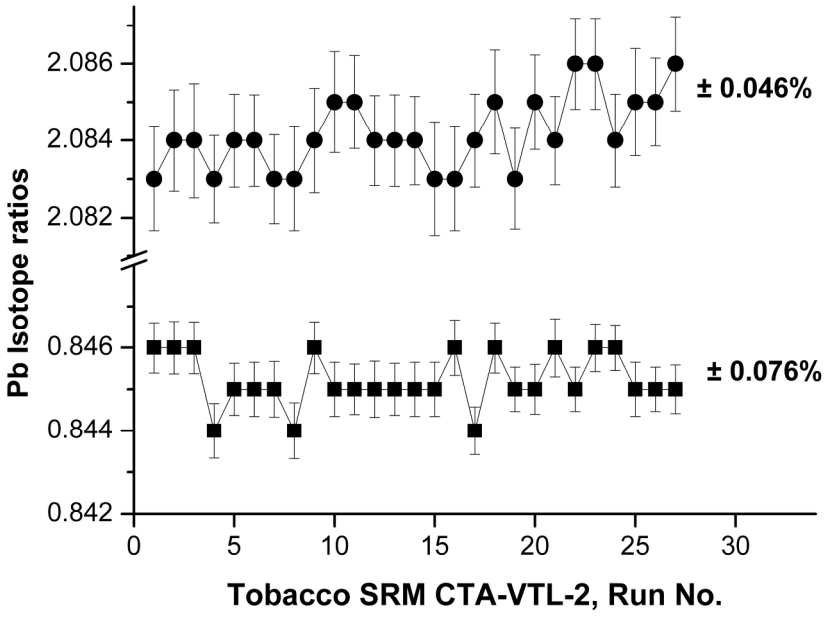

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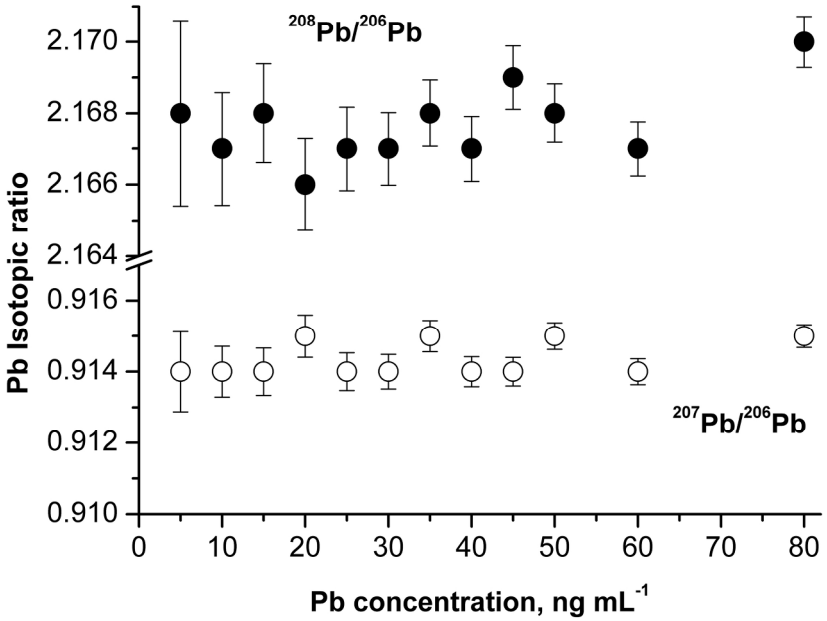
210x148mm (300 x 300 DPI)



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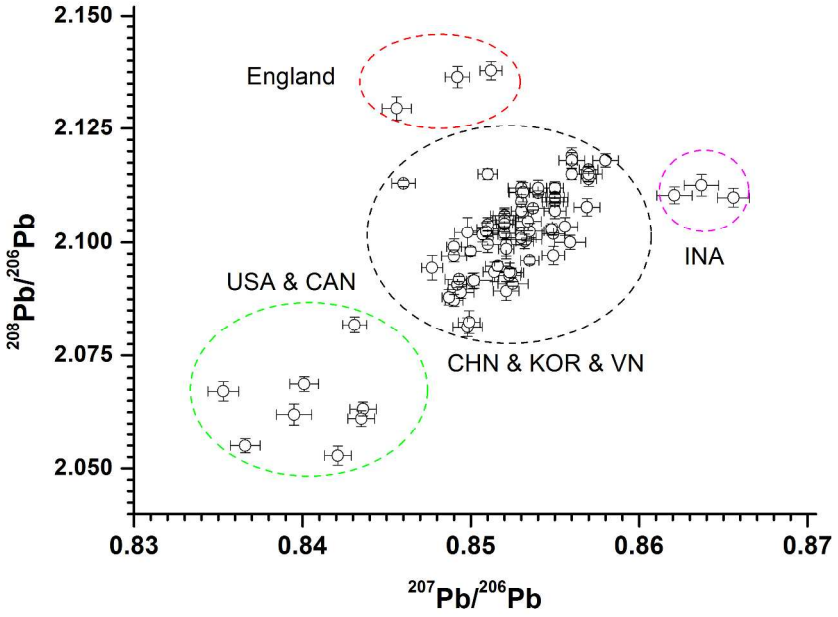

Figure 7 Results for lead isotope ratios in 91 different brands of cigarette originated from seven different countries, plot of $^{208}Pb/^{206}Pb$ against $^{207}Pb/^{206}Pb$.
297x210mm (300 x 300 DPI)