

ICP-MS determination of lead isotope ratios in legal and counterfeit cigarette tobacco samples

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A method for the determination of Pb isotope ratios (IR) in cigarette tobacco by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) has been developed and applied to tobacco samples from genuine and counterfeit cigarettes obtained in the USA. The IR $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ were measured using a Q-ICP-MS instrument. Two certified reference materials, grown in the USA and Bulgaria, were also analysed for comparison with the tobacco samples, as were tobacco samples from cigarettes obtained in Pakistan and China. The precision of the results was sufficient to distinguish between the counterfeit and genuine USA cigarettes. All of the genuine cigarettes and both reference materials, grown in different regions, were statistically distinct based on the measured ratios. The counterfeit cigarettes were indistinguishable from the reference material grown in Bulgaria. The technique shows promise as a method for identifying counterfeit cigarettes, possibly determining the source region.

Keywords: tobacco; cigarettes; lead; ICP-MS; counterfeit; forensic; isotope ratio; Pb isotope ratios; isotope measurements, methods and equipment; heavy isotopes; radioactive nuclides

1. Introduction

In recent years, there have been large numbers of counterfeit cigarettes sold in the USA, the UK, and other countries [1,2]. Counterfeit sales accounted for an estimated 15 % of cigarette sales in the UK in 2003–2004 [2]. The extent of cigarette smuggling into the USA is currently unknown, but federal agencies consider it a significant problem [3]. The largest producer of counterfeit cigarettes currently is China, which is the world's largest producer of tobacco and the largest consumer of cigarettes; another source region is in eastern Europe, especially the Balkan region [1].

It is well established that cigarette smoke presents a health hazard to both the smoker, who inhales the mainstream smoke, and to others in the vicinity who inhale the sidestream smoke. Tobacco-related illnesses are the leading cause of preventable deaths in the USA. Cigarette smoking results in approximately 440,000 annual deaths in the USA [4] and currently about 5.4 million globally [5].

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The majority of known carcinogens in cigarettes are organic compounds, but there are also several trace metals present which present a health hazard, such as cadmium, mercury, and lead. The health effects of these metals in cigarette smoke have not been thoroughly studied at this time [6]. Some of these trace metals possess chemical toxicity and/or can act as tumour promoters in combination with other carcinogens [7]. Fowles and Dybing [8] estimate that metals contribute at least 18 % of the cancer risk from smoking, and also contribute substantially to the non-cancer risk. Several studies have shown that the concentrations of many trace metals are higher in counterfeit cigarettes than in genuine brands; some may be present in concentrations several-fold higher [6,9,10]. Smoking counterfeit cigarettes may therefore present an even greater health hazard than smoking legal cigarettes [10].

In addition, the sale of counterfeit cigarettes presents a significant loss of tax revenues for the countries affected by this trade. From both public health and law enforcement perspectives, it is thus desirable to be able to distinguish counterfeit from legal cigarettes, and if possible determine the region of origin. Ng *et al.* [11] have proposed a technique for distinguishing between counterfeit and genuine cigarettes that uses electrospray ionisation-ion trap mass spectrometry. This method relied on the different ratios of certain organic compounds in three different varieties of tobacco: Virginia, burley, and Oriental. That technique can be used to distinguish between cigarettes based on the blend of tobaccos used, but does not provide information on the geographic origin of the tobaccos. More recently, the same laboratory reported measurements of $^{15}\text{N}/^{14}\text{N}$ and $^2\text{H}/^1\text{H}$ ratios of nicotine in genuine Canadian, American, and Chinese cigarettes, as well as some Canadian and American counterfeits. They found that the combined $\delta^2\text{H}$ and $\delta^{15}\text{N}$ values could be helpful in distinguishing between genuine branded Canadian cigarettes and the others, although there was some overlap between the different types [12].

In this paper, we investigate the possibility of distinguishing between genuine and counterfeit cigarettes and, if possible, determining the geographic region in which the tobacco was grown, using lead isotope ratios (IR). Our purpose is to develop a technique which is rapid, yet sensitive and precise enough to be helpful in determining the origin of cigarettes.

The trace metals present in plant tissues depend on the geographical region where they were grown. Plants accumulate trace metals from the soil in which they are grown, and also from substances deposited on the foliage. Trace elements are generally taken up with the same isotopic abundance as is present in the source material. Thus, isotope abundance ratios can provide powerful indicators of the geographic origin of products derived from vegetative matter [13]. If the geographic origin of the tobaccos used in counterfeit cigarettes is different from those used in the genuine ones, the lead IR in the two types would be different and could provide a means to distinguish between them.

Thermal ionisation mass spectrometry (TIMS) is generally considered the method of choice for heavy element IR measurements. Recently, however, improvements in instrumentation have made some IR measurements practical using inductively coupled mass spectrometry (ICP-MS). An advantage of using ICP-MS for IR is the much lower labour involved. Magnetic sector ICP-MS spectrometers are generally used for IR measurements. Multicollector models can rival TIMS for precision and accuracy [14,15], but are quite expensive. Quadrupole ICP-MS (Q-ICP-MS) spectrometers are much less expensive, and are in use in many more laboratories, but have lower precision than magnetic sector instruments, and have therefore not been commonly used as much for IR measurements. With improvements in instrument design, however, there has been an increase in the number of IR experiments performed with Q-ICP-MS.

All ICP-MS instruments exhibit some drift and mass bias; the bias impacts the IR measurements less at the heavy end of the mass spectrum, since the difference in isotope masses is lower relative to the ion mass. There are isobaric atomic and molecular interferences in plasma spectrometers, and quadrupole instruments have more limited resolving power than magnetic sector instruments

to separate these signals from the analytes. In general, there are more of these interferences at the lower masses in environmental samples [16]. In many cases, chemical separation of the analytes from the interferences in sample preparation or introduction is necessary to obtain useful results [17]. Lead has few likely isobaric interferences and exhibits large variations in IR, indicating that it may be a good candidate for IR identification and provenancing of plant materials via Q-ICP-MS.

Lead has been measured in tobacco leaves in various regions by several authors. In genuine branded cigarettes, lead concentrations are typically around $0.5 \mu\text{g/g}$, while in counterfeit cigarettes it may be 5–10 times higher [6,9,10]. The solutions resulting from digesting tobacco samples have sufficiently high concentrations of lead to perform IR measurements.

Lead has four naturally occurring stable isotopes, ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb . The only non-radiogenic isotope is ^{204}Pb ; the other three are the end products of radioactive decay of ^{238}U , ^{235}U , and ^{232}Th , respectively [18]. The $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values are commonly used in comparing environmental samples since the total lead concentrations are often low and the relative abundances of these three isotopes is much higher than that of ^{204}Pb . The relative abundances of these isotopes vary with the type and geological ages of the rocks and ore deposits at different sites, and hence with geographic locations [18].

The isotopic composition of lead in soils is not solely determined by the underlying regolith. Even if weathering were the only source of lead in soils, various chemical and physical processes in the weathering of rocks would lead to some differences between the lead IR of the soil and the underlying geology. More importantly, there are several other inputs to the lead content of soils. Fossil fuel burning for energy production is still a source of lead in atmospheric aerosols, which are transferred to the soil. The lead present in these aerosols also possesses regional signatures on varying spatial scales. Coal from different deposits has differing isotope signatures [19], as do crude oil deposits in different geographic regions, and the fuels that are produced from them [20]. Hard rock mining may also be a source of lead on a local to regional scale. Again, different ores will have different isotopic signatures [21]. The application of fertilisers may also add lead to soils. Since fertilisers from varying sources may be used on croplands, this contribution of lead may vary in isotopic composition on a more rapid timescale than the others.

The lead in soils in tobacco producing regions will be determined by all of the above inputs. The largest part of the environmental lead burden currently is from the earlier burning of leaded gasoline. Since the use of lead compounds as gasoline additives has been phased out, levels of lead in atmospheric aerosols have fallen dramatically [22,23]. The implementation of emissions regulations of coal and oil burning power plants has also contributed to this trend. Nonetheless, the accumulated deposits from these sources remain in the soils and will probably remain the largest source for decades at least.

Tobacco plants will take up lead from the soil, as well as from wet and dry deposition on the foliage, so the isotopic composition will reflect some combination of these sources. If the soil component dominates, the tobacco should have an isotope composition that reflects it. If the atmospheric component is significant relative to that from the soil, it may be a slowly varying regional signal from power plants or other sources, and the IR in the tobacco would still have a regional correspondence.

In addition to tobacco, there are over 500 different substances that cigarette manufacturers add to their products. Most of these are added in low amounts ($<0.1\%$), so if they only contain lead at trace levels, it should not affect the overall IR to a great degree. Since the tobacco industry considers the exact blends of ingredients in their products to be proprietary trade secrets, and does not disclose them, it is not possible at this time to discern whether this is in fact the case. On the other hand, cigarette manufacturers have rigorous quality control and try to keep their brands as consistent as possible, in order to maintain brand loyalty among consumers, and this may result in the lead isotope signatures of legal cigarettes being consistent for a given brand.

Several recent studies have used ICP-MS for measuring lead IR in order to identify the origins of various types of samples including wines [24], Chinese traditional medicines [25], and atmospheric aerosols [23,26,27].

2. Experimental

2.1. Cigarette samples

Five sets of cigarettes were initially received by our laboratory from the New York State Department of Taxation and Finance for trace metals analysis described elsewhere [9]. Two sets were genuine-brand cigarettes: (1) Marlboro Gold Virginia Stamped and (2) Marlboro Red Virginia Stamped; and three sets were cigarette samples identified as counterfeit: (1) Marlboro Red stamp H0631, (2) Marlboro Gold-wrapped and (3) Marlboro Gold-unwrapped. At a later date we also received cigarette samples from colleagues who were travelling overseas, two from Pakistan: (1) Capstan and (2) Pine Lights brands, and one from China, Liqun brand.

2.2. Standards and reference materials

Nitric acid 70%, Ultrex II ultra pure reagent grade from J.T. Baker (Phillipsburg, NJ, USA), and hydrogen peroxide 30–32%, from Aldrich Chemical Co. (Milwaukee, WI, USA), were used without further purification. Deionised distilled water (DDW), resistivity 18.2 M Ω cm, was used for all preparations. Two certified reference materials were analysed for comparison with the cigarette samples, CTA-VTL-2 Virginia Tobacco Leaves from the Institute of Nuclear Chemistry and Technology (INCT), Warsaw, Poland, and SRM 1573a Tomato Leaves, from the National Institute of Standards and Technology (NIST), Gaithersburg, MD. An isotopic standard solution (1000 mg/l) was prepared from NIST SRM 981 Natural Lead (Isotopic) by dissolving a portion of the metal in 10% v/v nitric acid. Standard solutions were prepared daily from the stock solution by dilution in 1% v/v Ultrex nitric acid.

2.3. Sample digestion

The details of the digestion procedure are described elsewhere [9]. In brief, the samples of cigarette tobacco (0.5–0.8 g) and reference materials (0.5 g) were placed in polytetrafluoroethylene (PTFE) digestion vessels with 2.0 ml of HNO₃ and 4.0 ml H₂O₂, and digested in a high-pressure microwave system CEM Model MARS 5 (CEM Corporation, Matthews, NC, USA). A two-step digestion procedure was used in order to prevent excessive pressure build-up in the digestion vessels.

Step 1 The temperature was ramped to 110 °C (maximum pressure 300 PSI) within 20 min with the application of 600 W power, followed by a dwell time of 5 min at 110 °C and an initial cooling in the microwave oven for 5 min. The vessels were then removed from the oven and cooled in a freezer at –20 °C for 1 h, after which they were vented and closed.

Step 2 The temperature was ramped to 200 °C (maximum pressure 350 PSI) within 10 min with the application of 1200 W power, followed by a dwell time of 10 min at 200 °C. They were again cooled in the microwave oven for 5 min and in a freezer at –20 °C for 1 h. After the final cooling, the digestate was quantitatively transferred to polyethylene sample tubes and the volume made up to 25 ml with DDW. This procedure provided an excellent lead recovery for CTA-VTL- 2 (105 ± 4%, $n = 7$).

2.4. Inductively coupled plasma mass spectrometry

The samples were analysed on an Agilent 7500ce ICP-MS (Agilent Technologies, Palo Alto, CA, USA), equipped with Chemstation Software and an Agilent ASX 500 autosampler. The instrument was equipped with a peristaltic pump, concentric nebuliser (Glass Expansion, Poasset, MA, USA), and nickel sampler and skimmer cones. The instrument was optimised daily, using a solution containing 1 $\mu\text{g/l}$ Li, Y, Ce and Tl. The three isotopes ^7Li , ^{89}Y and ^{205}Tl were monitored, and the sensitivity and precision in all three masses were optimised in order to obtain a flat response curve, which is desirable for IR analyses. While we did not specifically tune the instrument to reduce oxides, the benchmark value of $^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce}$ was generally below 2%. Oxide interferences in the mass range 202–208 are not likely, since this would require significant levels of W, Os, or Pt in the tobacco samples.

An interference correction was applied to the ion counts for ^{204}Pb to correct for any Hg present. The signal at m/z 202 was multiplied by 0.2301 (the natural abundance ratio of $^{204}\text{Hg}/^{202}\text{Hg}$) and the result was subtracted from the signal at m/z 204 ($^{204}\text{Pb} + ^{204}\text{Hg}$). Subsequent measurements of several mercury solutions indicated that the ratio measured with this instrument is somewhat higher, 0.2399; using this value would result in changes of less than 0.07% in all the ratios. A relatively high radio frequency (RF) power (1600 W) was used in order to minimise any matrix effects. Typical instrument operating parameters are shown in Table 1. The ion sensitivity was around 100,000 counts per second for ^{208}Pb for a 1 $\mu\text{g/l}$ solution. Since the instrument manufacturer recommends keeping the ion counts below 800,000 cps for IR measurements in order to avoid detector dead time affecting the measurement, the tobacco samples were diluted to approximately 5–6 $\mu\text{g/l}$ before analysing. The Pb concentrations in the tomato leaf reference material digests were already below this and were used without further dilution.

We investigated the effect of integration time on the precision of the IR measurements. Our goal was to obtain sufficient precision while keeping the analysis time to the minimum necessary to accomplish this. Based on the instrument manufacturer's recommendation, we acquired 10 replicate measurements with short individual integration times. Figure 1 shows the relative precision, expressed as relative standard deviation (RSD) of the IR measurements of a 5 $\mu\text{g/l}$ standard solution with increasing integration time. The x -axis is the integration time for the ^{208}Pb isotope. The integration times for the ^{206}Pb , ^{207}Pb and ^{204}Pb isotopes were set two, two and four times as long, respectively, due to the relative abundances of the isotopes. We elected to use a 0.4 s acquisition time for the ^{208}Pb isotope, since the precision versus integration time curve appeared to level off at this point. We did not investigate the effect of acquisition times longer than 0.5 s, since the precision of the ratios of the higher abundance masses at this setting was similar to values that had been reported in the literature for quadrupole instruments. Yoshinaga [28] found no increase in precision for acquisition times longer than 2–3 s on an Agilent 4500 ICP-MS instrument. Current ICP-MS spectrometers are about 10 times more sensitive and more stable, and attain maximum precision at somewhat shorter integration times. More recently, Moretti *et al.* [29] used similar acquisition times for the ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes with a much longer integration time for the 204 mass (19 s); they obtained similar precisions to ours for the IR. The total analysis time for our method was about 5 min/sample.

Table 1. ICP-MS operating parameters.

RF power	1600 W
RF matching	2.0 V
Sample depth	8.2 mm
Carrier gas	1.121 min^{-1}
Blend gas	0.051 min^{-1}
PeriPump	0.10 rps
S/C Temp	2°C

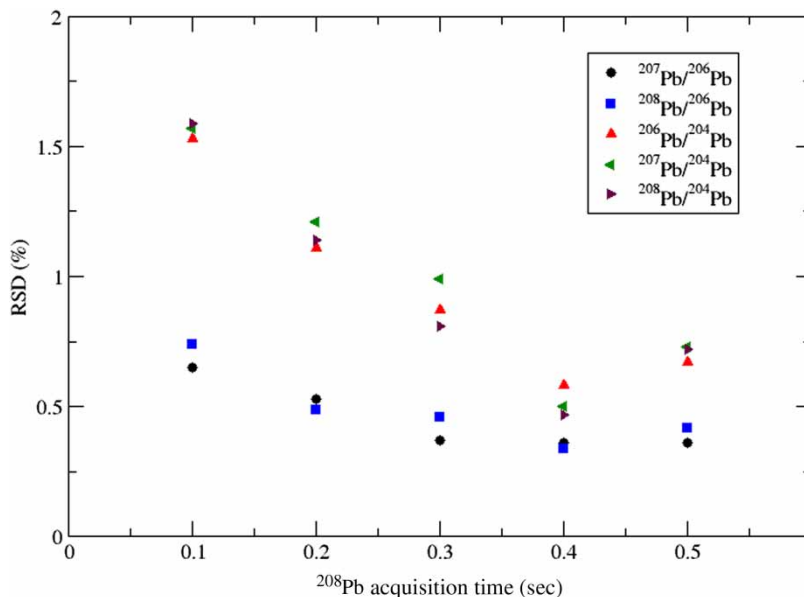


Figure 1. Lead IR precision versus ^{208}Pb acquisition time. The acquisition times of the other isotopes varied due to differences in the natural abundances.

3. Results and discussion

3.1. Precision and sensitivity

Q-ICP-MS instruments are known to exhibit some mass bias and instrument drift. We accounted for this using an external sample/standard bracketing method. A solution of NIST SRM 981 at a concentration of $5\ \mu\text{g}/\text{l}$ was analysed at the beginning and end of each run, and after every fifth sample. This method gives good results when the matrices of the samples are well matched with the standard [30,31]. Internal correction using a thallium spike and fractionation expressions has also been used to correct for mass bias in lead ratio measurements [32,33]; both methods generally give adequate results. An advantage of the bracketing technique is that the same masses are measured for the correction as in the ratio measurement; mass bias can vary slightly even among neighbouring masses.

A mass bias correction factor was calculated for each NIST analysis

$$\alpha = \text{IR}_c / \text{IR}_m,$$

where IR_c is the certified IR and IR_m the measured ratio. This factor, linearly interpolated over the acquisition times, was used to correct the measured ratios in the tobacco and tomato leaves reference materials, and the genuine and counterfeit cigarette tobacco samples. The correction factor varied from 0.9922 to 1.0061 for $^{207}\text{Pb}/^{206}\text{Pb}$, 0.9838 to 1.0006 for $^{208}\text{Pb}/^{206}\text{Pb}$ and from 0.9686 to 1.0015 for the ratios using ^{204}Pb .

The analyses of NIST 981 also provided a record of the stability of the measurements over the course of the experiments. The uncorrected values of the SRM 981 IR for a series of analyses, which occurred on several days over a period of about 11 months, are shown in Figures 2a and b. Figure 2a shows the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values, and Figure 2b shows the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values. Ion counts for the blanks ranged from 0.1 to 0.6 % of the sample counts for all masses and did not significantly alter the ratios. The dotted lines are the mean values of the measured ratios, and the solid lines are the certified values. There is a slight

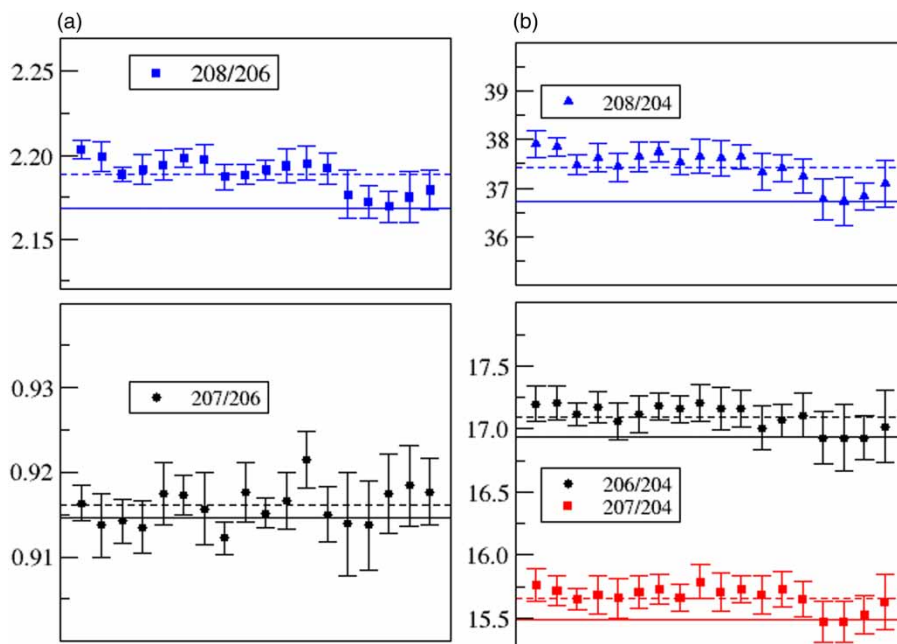


Figure 2. Lead IR measurements of NIST SRM 981. The solid lines are the certified values, the dotted lines are the means of the measurements, and the error bars are equal to \pm one standard deviation. The measurements took place on four separate days over a total span of several months.

Table 2. NIST SRM 981 IR measurements.

Ratio	Measured	Certified
$^{207}\text{Pb}/^{206}\text{Pb}$	0.9154 ± 0.0023	0.91464 ± 0.00033
$^{208}\text{Pb}/^{206}\text{Pb}$	2.194 ± 0.0057	2.1681 ± 0.0008
$^{206}\text{Pb}/^{204}\text{Pb}$	17.16 ± 0.0293	16.94 ± 0.015
$^{207}\text{Pb}/^{204}\text{Pb}$	15.71 ± 0.0277	15.49 ± 0.013
$^{208}\text{Pb}/^{204}\text{Pb}$	37.65 ± 0.597	36.72 ± 0.013

positive bias in all of the ratios, ranging from 0.2 % for $^{207}\text{Pb}/^{206}\text{Pb}$ to 2.7 % for $^{208}\text{Pb}/^{204}\text{Pb}$. The long-term stability of the measurements over this time period is excellent. Table 2 lists the means and confidence levels ($p = 0.05$) of 10 measurements of the five ratios, along with the certified values.

3.2. Reference materials and tobacco samples

Aliquots of digestate were taken from four or five samples each of NIST 1573a Tomato Leaves, CTA-VTL-2 Virginia Tobacco Leaves, counterfeit and genuine cigarette samples, and analysed as described above, representing tobacco grown in several different geographic regions. The NIST 1573a SRM was grown in Rock Springs, Pennsylvania, USA, the INCT CTA-VTL-2 was grown in Bulgaria, the Marlboro cigarette tobacco was grown in the southeastern USA and the Liqun cigarette tobacco was grown in China, while the sources of the Captstan and Pine Lights, which were purchased in Pakistan, and the counterfeit tobacco leaves, are unknown.

The results of the sample analyses are shown in Table 3. The concentrations are as analysed; all the tobacco digests were diluted to match the tomato leaves and limit the counting rate as discussed

Table 3. IR results.

Sample	Total lead ($\mu\text{g/l}$)	$^{207}\text{Pb}/^{206}\text{Pb}$		$^{208}\text{Pb}/^{206}\text{Pb}$		$^{206}\text{Pb}/^{204}\text{Pb}$	
		Mean	% RSD	mean	% RSD	mean	% RSD
1573a #1	5.78	0.8265	0.43	2.028	0.36	19.00	0.72
1573a #2	5.39	0.8253	0.33	2.030	0.39	18.94	0.84
1573a #3	5.75	0.8235	0.24	2.020	0.44	18.98	0.76
1573a #4	5.48	0.8227	0.15	2.020	0.44	19.05	0.94
1573a #5	5.43	0.8237	0.26	2.022	0.17	18.95	0.76
CTA-VTL-2 #1	4.71	0.8447	0.44	2.090	0.42	18.63	0.55
CTA-VTL-2 #2	4.70	0.8449	0.39	2.090	0.28	18.61	0.66
CTA-VTL-2 #3	4.58	0.8414	0.50	2.081	0.34	18.62	0.64
CTA-VTL-2 #4	4.91	0.8444	0.27	2.093	0.28	18.59	0.62
CTA-VTL-2 #5	4.47	0.8455	0.22	2.088	0.26	18.50	0.67
Marlboro #1	4.77	0.8329	0.40	2.052	0.47	18.87	1.02
Marlboro #2	5.32	0.8348	0.30	2.056	0.41	18.79	0.71
Marlboro #3	5.81	0.8354	0.42	2.058	0.26	18.81	0.94
Marlboro #4	5.22	0.8326	0.29	2.052	0.31	18.95	0.63
Marlboro #5	5.95	0.8318	0.33	2.049	0.30	18.90	0.58
Counterfeit #1	4.84	0.8440	0.53	2.087	0.50	18.52	0.78
Counterfeit #2	5.37	0.8446	0.24	2.088	0.31	18.67	0.51
Counterfeit #3	4.93	0.8472	0.31	2.095	0.36	18.59	0.70
Counterfeit #4	5.01	0.8460	0.31	2.086	0.36	18.55	0.84
Counterfeit #5	4.95	0.8488	0.24	2.096	0.32	18.50	0.96
Liquan #1	4.83	0.8521	0.22	2.223	0.25	21.91	1.46
Liquan #2	4.55	0.8507	0.13	2.218	0.23	22.57	0.90
Liquan #3	4.33	0.8496	0.21	2.215	0.48	22.91	0.59
Liquan #4	4.64	0.8528	0.26	2.222	0.26	21.77	1.08
Capstan#1	4.67	0.8581	0.35	2.091	0.41	18.01	1.96
Capstan#2	4.59	0.8574	0.32	2.092	0.39	18.09	2.86
Capstan#3	4.89	0.8587	0.32	2.095	0.34	18.11	2.34
Capstan#4	4.90	0.8556	0.35	2.092	0.23	18.23	1.97
Pine Lights #1	4.60	0.8450	0.37	2.073	0.38	18.44	1.31
Pine Lights #2	5.19	0.8456	0.48	2.076	0.48	18.38	0.78
Pine Lights #3	4.36	0.8460	0.21	2.076	0.27	18.43	1.40
Pine Lights #4	4.93	0.8431	0.23	2.070	0.37	18.44	1.05

above. The $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios can be derived from those shown in the table. Each measurement is the mean of 10 replicates. The RSDs range from 0.15–0.48 % for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, and from 0.25 to 2.97 % for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios. Almeida *et al.* [24] reported similar uncertainties for the more abundant isotopes in Q-ICP-MS lead IR measurements on port wine samples, as did Margui *et al.* [21] in vegetation samples. Since only the total lead value is certified in the reference materials, the accuracy of the IR measurements in the tobacco standards and samples cannot be assessed at this time.

The sample types fall into five distinct groupings based on the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values, as shown graphically in Figure 3. Each point represents one sample; the error bars are the standard deviation of each measurement (10 replicates). The ellipses are drawn with major and minor axes equal to the 95 % confidence intervals for each sample type; this is the total uncertainty in the ratios, including both the instrument precision and the variation in the samples. The NIST 1573a, Marlboro, Capstan and Liquan samples are all statistically distinct from each other based on these ratios, and from the fifth group, which contains the counterfeit cigarettes, the CTA-VTL-2 tobacco leaves and the Pine Lights cigarettes. The $^{207}\text{Pb}/^{206}\text{Pb}$ IR are statistically different at the $p = 0.01$ level between each group, and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios differ at the $p = 0.05$ level or better. The $^{208}\text{Pb}/^{206}\text{Pb}$ values in the Liquan cigarettes are about 10 % higher than the other

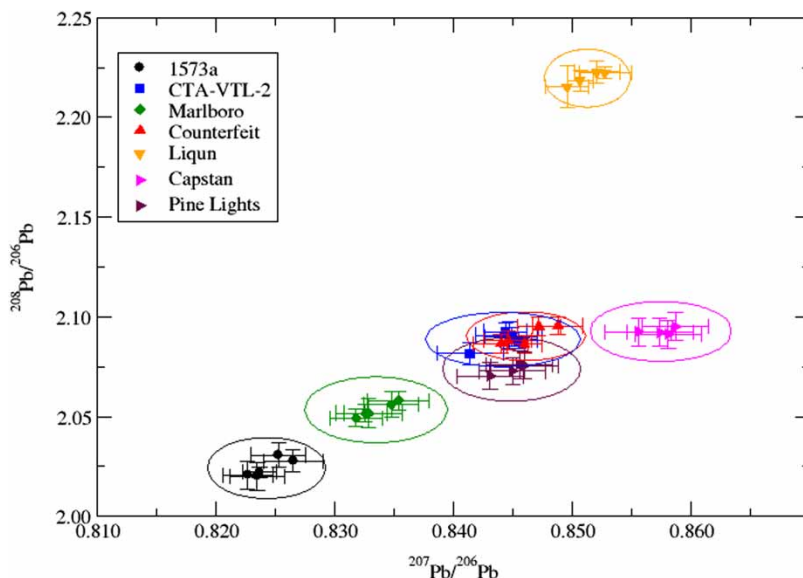


Figure 3. $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ IR for legal and counterfeit cigarettes, NIST SRM 1573a and tobacco SRM CTA-VTL-2. The axes of the ellipses represent the 95 % confidence intervals of the five measurements of each sample type.

samples; similar ratios have been reported in atmospheric aerosols derived from coal combustion and vehicle exhaust in Shanghai [26,34].

The sample group that contains the three sample types can be further discriminated using the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values. These ratios are not significantly different in the CTA-VTL-2 and counterfeit samples. In Pine Lights cigarettes, however, they differ from both the CTA-VTL-2 and counterfeit samples at the $p = 0.01$ level. The CTA-VTL-2 and counterfeit cigarettes are the only two sample types which are indistinguishable using the combined IR. Since the Balkan region is one source region of counterfeit cigarette tobacco, it is possible that the tobacco in the counterfeit samples, originates in the same region as the CTA-VTL-2 tobacco, but without many more samples for comparison, it is not possible to make an estimate of the likelihood of this.

4. Conclusions

We have developed a method for the digestion and subsequent lead IR measurement of cigarette tobacco samples via Q-ICP-MS. The method requires minimal sample preparation and allows rapid analysis times. The precision of the IR was less than 0.55 % for the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, and from 0.50–2.97 % for the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios.

The IR measurements had sufficient precision to distinguish between tobacco samples grown in four different geographic regions: genuine US branded cigarettes from the southeastern USA, NIST SRM 1573a tomato leaves from Pennsylvania, USA, INCT CRM CTA-VTL-2 Virginia tobacco leaves grown in Bulgaria and Liqun cigarettes from China. Two cigarette brands purchased in Pakistan, Pine Lights and Capstan, were also statistically distinct based on the IR. The counterfeit samples were indistinguishable from the CTA-VTL-2 SRM.

The method presented here is capable of distinguishing between the US branded cigarettes and the counterfeits in the small number of samples that we analysed. This technique shows promise as a forensic tool to determine the origin of cigarette tobaccos, but much further research is necessary to determine how well it can distinguish between tobaccos produced in different regions. A large

number of cigarette samples from different tobacco producing regions would have to be analysed to generate a useful geographic database of lead IR and determine the applicability of this technique. This database would probably need to be updated periodically due to changes in the lead IR from atmospheric deposition and other processes, although it is unclear at this time the time scale or magnitude of any changes that might occur. The use of a high resolution (single or multiple ion detector magnetic sector) ICP-MS spectrometer and/or combining IR of lead with concentrations or IR of other elements might also improve the ability to determine the geographic origin of different tobacco products.

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