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Direct Determination of Metals in Archaeological Artifacts by Fast Atom Bombardment Mass Spectrometry

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Direct analysis of lead-based glasses and glazes by fast atom bombardment mass spectrometry without a glycerol matrix is demonstrated as a convenient and rapid method for obtaining elemental compositions and lead isotope ratios. Data were collected with a double-focusing mass spectrometer and data system. Many elements including lead, copper, and iron were detected in 19th century American glazed ceramic sherds. Lead isotope ratios were measured to a relative precision ranging from 0.3 to 1% in the ceramic glazes and in a glass containing National Bureau of Standards SRM 981 "common" lead.

Archaeological chemistry is a relatively new field that has combined modern analytical methods with the classical techniques of archaeology. Several reviews of the advances in this field have been published (1, 2). Materials that have been uncovered by archaeological excavations present intriguing and difficult problems as samples for chemical analysis. Frequently, archaeological samples are highly complex mixtures of materials in which the species of analytical interest may be trace components. Sample sizes are usually very small due either to the small size of the archaeological object itself or to the object's large intrinsic value which would be reduced if a substantial section of it were destroyed for purposes of analysis. Techniques for analyzing archaeological samples need to be specific for a wide range of species and nondestructive or requiring small sample sizes. Also, since the number of archaeological samples that needs to be analyzed for a particular excavation can be quite large, the analytical method ideally should be rapid.

A number of instrumental techniques have been employed for the analysis of archaeological samples, including X-ray fluorescence (3), atomic adsorption (4), atomic emission (5), neutron activation (6), electron microprobe analysis (7), and thermal ionization mass spectrometry (8, 9). All of these techniques have been used for quantitative elemental analysis of archaeological samples. The relative concentrations of elements in the samples frequently can be used to determine the geographical origin of the artifacts (5). With mass spectrometry, it is possible to determine stable isotope ratios for many elements in archaeological samples. Certain elements, such as lead, have isotope ratios which vary according to the geological deposit in which they were formed (10). Lead isotope ratio data have been compiled for many sources of lead ore from around the world (10-13). Therefore, if one compares the lead isotope ratios from archaeological artifacts to the lead isotope ratios of lead ores from known locations, the origin of the lead in the artifacts can be determined. Lead is, in fact, a common element in a wide variety of archaeological samples including pigments, alloys, glasses, and glazes. Therefore, lead isotope ratio mass spectrometry is a powerful method for gaining insights into the place of origin of many archaeological artifacts (14-18).

Fast atom bombardment mass spectrometry (FAB-MS) is a new technique that has found many applications for analysis

of organic samples (19). In this technique solid or liquid samples are frequently dissolved in a viscous liquid matrix such as glycerol which is subjected to bombardment by 4-8 keV Ar or Xe atoms. From this solution, ions representative of both the matrix and the sample are produced. FAB-MS using a liquid matrix has not been used for inorganic elemental analysis due to interfering organic ions from the liquid matrix but FAB-MS has been used recently for solid samples (20). FAB-MS is similar to secondary ion mass spectrometry (SIMS), the main difference being that the primary beam is neutral, not charged (21). Since SIMS has been used extensively for organic and inorganic elemental analysis without a glycerol matrix (22), we explore the possible use of FAB-MS for similar purposes.

Certain "glasses" emit positive ions when heated (23). These materials are referred to as thermionic emitters. For example, a 1:1:2 mixture of $\text{SiO}_2\text{:Al}_2\text{O}_3\text{:K}_2\text{O}$ forms a glass when heated. If this glass is subsequently heated resistively in a mass spectrometer (and is positively biased), it emits potassium ions. It has been observed that such glasses also emit potassium ions when bombarded by fast atoms in the absence of any resistive heating (24). In fact, such a FAB ionization of thermionic "potassium glass" is capable of producing a K^+ ion signal that can saturate the electron multiplier of a double-focusing sector mass spectrometer. Since such instruments have inherently low ion-transmission efficiencies, FAB of thermionic emission glasses can be considered as a copious, stable source of ions (24).

A number of lead-glazed ceramic pottery sherds of archaeological significance have been donated to our laboratory for analysis (25). These pottery sherds are from Whitemarsh Township, PA, and date from the mid 1800s. The samples were excavated from the grounds of a country estate called the Highlands that had been built by Anthony Morris (25). The glazes on the pottery are primarily alumina and silica, with metal oxides added for color and as fluxing agents (26). They are very similar in composition to the thermionic emitters that have been described. These observations led to the development of lead thermionic emission glasses and to the use of FAB-MS for direct analysis of the 19th century ceramic glazes.

EXPERIMENTAL SECTION

Mass Spectrometer. The instrument used was a Varian MAT CH-5DF, a reversed Nier-Johnson geometry double-focusing mass spectrometer. The instrument is equipped with a combination electron impact (EI)/field desorption (FD)/field ionization (FI)/fast atom bombardment (FAB) ion source. An Ion-Tech, Ltd., Teddington, England, Model B11NF fast atom gun with a B-50 current-regulated power supply was mounted on the mass spectrometer at a distance of 11 cm from the center of the ion source and at an angle of 90° to the path of the sputtered ions which were mass analyzed. The mass spectrometer is equipped with two direct insertion probes, one for EI samples and the other for FD samples. The field desorption probe was modified slightly to accept FAB sample "targets". Both solid copper and aluminum tips fit the standard FD emitter base. The face of the FAB tip that holds the sample is machined such that the angle of incidence of the FAB beam was approximately 60° . All data were collected

with a PDP-8e minicomputer data system. Details of the data system have been published previously (27).

FAB Conditions. The standard experimental conditions for running nearly all FAB analyses in our laboratory are as follows: the FAB gun voltage is 8.0 kV; typical FAB gun current is 1.0 mA; the instrument operates at a mass resolution of 500 (5% valley); the accelerating voltage used is 2817 V; and the xenon pressure in the ion source is 1×10^{-5} torr. Modifications have been made to the FAB gun as suggested in a recent article by Martin et al. (28). These modifications include a smaller hole in the gun's front cathode, a blocked rear cathode, and a higher quality high-voltage connection.

Production of Lead Glass. Lead glasses were fabricated from a mixture of 0.1 mmol of lead nitrate, 0.1 mmol of alumina, and 0.2 mmol of silica. The ratio 1:1:2 was taken from an early paper on thermionic emitters (23). The composition of this glass is similar to the composition of the glass that produces K^+ ions (24). Lead nitrate is used as a source of lead, since, on heating, the lead nitrate decomposes to PbO which is desired for the glass. This mixture was ground to a fine powder in a mortar and pestle which had been cleaned with concentrated nitric acid, rinsed with distilled water, and dried with acetone. A small portion of the powder was placed in a platinum boat and carefully heated from the reverse side with an oxygen-acetylene torch until the powder was red hot. This procedure produces a rough uneven opaque glass. Another glass of the same composition was prepared, but with National Bureau of Standards (NBS) SRM 981 "common" lead (29) instead of reagent grade lead nitrate. The NBS lead was dissolved in analytical grade nitric acid and heated to dryness on a hot plate to form the lead nitrate, which was used to make the glass.

FAB Analysis of Lead Glasses and Archaeological Samples. The lead glasses were analyzed without further modification under FAB conditions. For the archaeological ceramics, a small chip of glaze (an average 1 mg) was carefully removed from the artifact with a razor blade and then weighed. The glaze chip was also used without modification as a FAB sample. Both the glasses and glazes were attached to the surface of the probe tip with a small square of two-sided cellophane tape. The samples were inserted through a vacuum lock into the ion source. The probe position and ion optics were adjusted to maximize the ion current at m/z 39 for potassium which was present in all samples; then several rapid magnetic scans of the mass range m/z 19 to m/z 500 were collected and averaged. The isotope ratios for lead were also obtained if lead was present in the sample. Isotope ratio data were collected by slow magnetic scanning with rapid data collection over the mass range m/z 203 to m/z 209. The areas under the peak for each isotope were integrated by using the data system (27).

Quantitative Analysis of Ceramic Glazes. To validate the FAB methodology, the same chips of ceramic glazes that had been used for FAB analysis were analyzed quantitatively for Pb, Fe, Cu, Mn, and Al by inductively coupled plasma emission spectrometry, using a Jarrell-Ash Model 955 Plasma Atomcomp. The glaze samples were wet ashed in 1 mL of concentrated nitric acid in a Teflon container at 80 °C for 24 h and diluted with 5 mL of distilled water. This procedure dissolves most materials except silicates. Since these samples are composed primarily of silicates, a residue remains undissolved, so the analysis is for total extractable metals.

RESULTS AND DISCUSSION

FAB Mass Spectra of Lead Glasses and Glazes. All of the FAB mass spectra in this paper were obtained directly from glasses and glazes without a glycerol matrix. A general feature of these spectra is that ion intensities are somewhat lower than are observed from glycerol, but the lead glasses that were prepared often gave useful spectra periodically for several weeks, even when used daily. Another general feature of these spectra is that atomic metal ions, M^+ , dominate the spectra although occasionally molecular ions such as MOH^+ are seen as well.

Figure 1a shows the FAB mass spectrum of a glass prepared from NBS isotopic standard 981 "common" lead which had been converted to lead nitrate and melted together with one

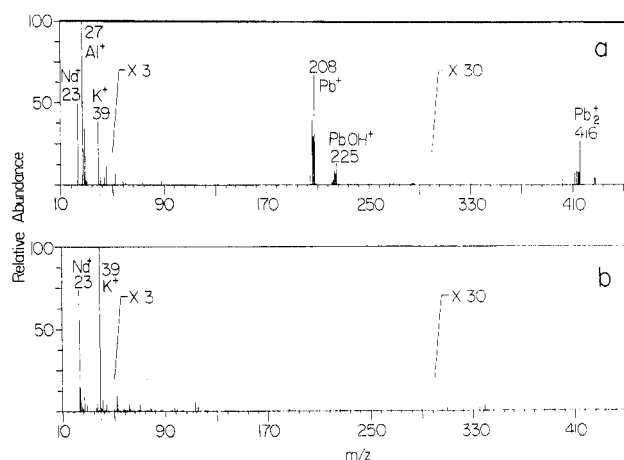


Figure 1. FAB mass spectrum: (a) of a glass prepared from alumina, silica, and NBS SRM 981 "common" lead; (b) of the background peaks in the mass spectrometer, including those from two-sided cellophane tape.

part alumina and two parts silica. The major peaks in the spectrum represent aluminum at m/z 27 and lead at m/z 204, 206, 207, and 208. Other prominent peaks include Si^+ at m/z 28, Na^+ at m/z 23, and K^+ at m/z 39 and 41. If the scale in Figure 1a is expanded, it is possible to observe two other peaks in the lead isotope cluster at m/z 205 and 209. Exact mass measurement of the ion current at nominal mass 209 indicates that the species was PbH^+ (measured value 208.985 amu, calculated value 208.984 amu).

In principle, one could measure the ratio between the intensity of the m/z 204 peak of Pb^+ and the intensity of the m/z 205 peak of PbH^+ and correct the measured lead isotope abundance ratios for the presence of PbH^+ at m/z 207 and 208. In practice, it is very difficult to measure the intensity of the m/z 204 peak precisely, and frequently the m/z 205 peak cannot be measured at all. Clearly this isotopic interference limits the accuracy of the isotope measurements that one can make with this method. Fortunately, the PbH^+ intensity from the glass is very low and the most important isotope ratio from an archaeological standpoint, the $^{204}Pb^+/^{206}Pb^+$ ratio, is unaffected by the PbH^+ interferent.

In the mass spectrum in Figure 1a, clusters of peaks at masses higher than lead are also observed. The clusters whose highest mass peaks are at m/z 225 and m/z 416 are $PbOH^+$ and Pb_2^+ , respectively. Metal clusters of this kind have been reported previously in SIMS (30) and in FAB-MS (28). Suggested elemental compositions for the major ions in all the mass spectra appear in the figures. Unfortunately it is extremely difficult to identify most of these ions by their exact mass, due to a lack of ions in the glass that could be used as peak matching standards except for potassium and lead.

Background from Adhesive Tape in Sample Mount.

As previously indicated most of the ceramic archaeological samples were mounted on the FAB probe tip with two-sided cellophane tape. When the sample was fairly large (3 mm \times 6 mm) such as the lead glass in Figure 1a, the tape was hidden entirely behind the sample, but occasionally, when working with chips that were very small (approximately 1 mm in diameter), portions of the tape were also bombarded. In these cases the FAB beam produced ions from the tape as well as from the sample. Figure 1b shows the spectrum of two-sided tape. Fortunately, the intensity of ions from the tape diminishes quickly with time, whereas the signal from the ceramic glazes stays nearly constant or even grows slightly with time. Even so, it is possible to observe some of the more persistent ion currents from the tape such as ions at m/z 113 and 115 in some of the ceramic FAB mass spectra. In no case, fortunately, did ions from the tape interfere with measuring

Table I. ICPAES Multielement Analysis of Ceramic Glazes

sample	concentration, ^a ppm				
	Pb	Fe	Cu	Mn	Al
lead-glazed redware	3700 (Y)	3800 (Y)	(N) ^b	(N) ^b	2700 (Y)
manganese-glazed redware	1900 (Y)	3000 (Y)	(N) ^b	(Y) ^b	1700 (Y)
slipware (red section)	4700 (Y)	7100 (Y)	(N) ^b	(N) ^b	5400 (Y)
pearlware	(N) ^b	(N) ^b	(N) ^b	(N) ^b	900 (Y)
slipware (green section)	5600 (Y)	6800 (Y)	200 (Y)	(N) ^b	3800 (Y)

^a Y or N in parentheses indicates if the element was found by FAB-MS in the same sample. ^b Not detected in sample by ICPAES.

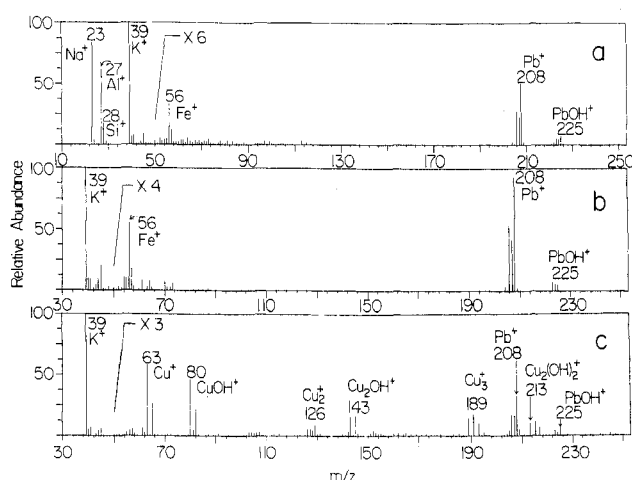


Figure 2. FAB mass spectra of chips of glaze from the following 19th century ceramics: (a) lead-glazed redware; (b) red section of lead-glazed slipware; (c) green section of lead-glazed slipware.

the intensities of the lead isotopes.

Lead-Glazed Redware by FAB. Figure 2a is the mass spectrum of a piece of lead-glazed redware. The color of the glaze is deep red. The Pb^+ and $PbOH^+$ isotopic clusters are apparent at m/z 204–208 and m/z 221–225, respectively. At low mass, the ions Na^+ , Mg^+ , Al^+ , Si^+ , K^+ , and Fe^+ are also present. There is a large number of very small peaks between m/z 50 and m/z 120. These may be ions from the two-sided tape, elemental species, or other compounds in the glaze. For this reason it is difficult to identify any peaks in this region for most of the ceramics, except where certain peaks are much larger than the rest. Fortunately, most metals in the glazes tend to exhibit intense ion signals and are easily recognizable.

Lead-Glazed Slipware by FAB. This pottery sample has a red glaze on it with a decorative green pattern called a slip. Figure 2b shows the mass spectrum of the red section and Figure 2c shows the mass spectrum of the green section. Surprisingly, both mass spectra indicate the presence of lead. The mass spectrum of the red section has prominent peaks at m/z 56, 40, and 39, which are Fe^+ , Ca^+ , and K^+ , respectively. The mass spectrum of the green section of the glaze contains, in addition to K^+ , Pb^+ , and $PbOH^+$, a number of other peaks starting at m/z 63 and m/z 65. The m/z values and abundance ratio of this pair indicate Cu^+ . The other peaks in the spectrum represent copper compounds or copper clusters such as $CuOH^+$ and Cu_2^+ . It seems likely that copper present in the glaze is the cause of its green coloration. Since lead was found in both the red and green sections of the glaze, it apparently has little effect on the color of the glaze. The red coloration, therefore, is probably due to the iron present in the glaze.

Pearlware and Manganese-Glazed Redware by FAB. We also received some artifacts that were considered to contain lead. Among these were some samples of pearlware and manganese-glazed redware. Figure 3a is the mass spectrum of a piece of pearlware body sherd. Pearlware, indeed,

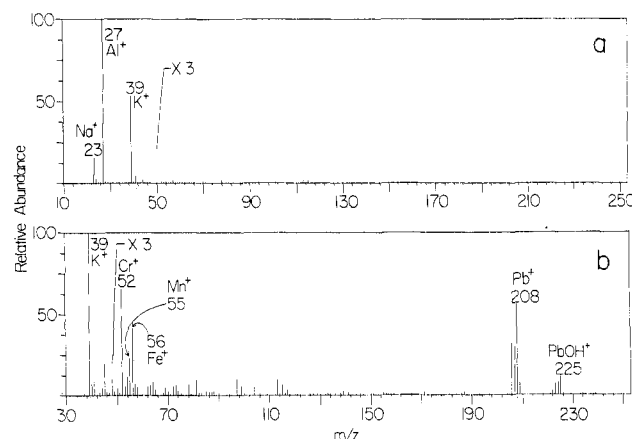


Figure 3. FAB mass spectra of the following glazed ceramics assumed to contain little lead: (a) pearlware; (b) manganese-glazed redware.

contains no lead, nor, apparently, any other metal with an atomic weight greater than m/z 50. Figure 3a shows all of the typical ions lower in mass than m/z 39 (K^+) but the intensity of the Al^+ peak is very large in comparison to the K^+ peak which is usually the base peak. Figure 3b is the mass spectrum of a piece of manganese-glazed redware. It has major peaks at m/z 52, 55, and 56 indicating the presence of Cr^+ , Mn^+ , and Fe^+ . Pb^+ at m/z 204–208 is also present.

It appears that lead is a common element in these pottery glazes, even in the pottery that archaeologists generally suppose contains little lead. By the 19th century, people began to realize that lead was poisonous (31) but substantial amounts of lead apparently were still present in their pottery according to the FAB-MS data. An extensive survey of lead-glazed pottery and other types of glazed ceramics from that period might have interesting historical implications if lead were in fact present in a wide variety of pottery as recently as a century ago. FAB-MS of the pottery sherds is nonquantitative and considerable effort would have to be expended to establish it as a quantitative tool, although in principle, this could be done.

ICP Results for Ceramic Pottery Glazes. In order to obtain a parallel, quantitative evaluation of the elements in the glazes, small portions of the glazes were analyzed by inductively coupled plasma atomic emission spectrometry (ICPAES). The results of the ICPAES analyses are given in Table I. The ICPAES data agree qualitatively with the FAB-MS data for all the elements analyzed except for Mn, which was not detected by ICPAES in any of the samples. Since any manganese present in the glazes is probably in the form of manganese dioxide which is insoluble in nitric acid, it is likely that the solution analyzed by the ICPAES contained virtually no Mn. The ICPAES data also show that lead and iron are by far the most common extractable elements from the glazes, and copper, indeed, is a constituent of the green slip. Presumably silica, which, of course, did not dissolve, composes the bulk of the glaze. Lead is seen to be present in large quantities in all the glazes except the pearlware.

Table II. Lead Isotope Ratios and Standard Deviations by FAB-MS and NBS Methods

Pb isotope ratios	NBS certified values for SRM 981	FAB-MS internal precision	FAB-MS external precision
204/206	0.05904 ± 0.00004	0.0575 ± 0.0002	0.0569 ± 0.0007
207/206	0.9146 ± 0.0003	0.935 ± 0.002	0.943 ± 0.006
208/206	2.1681 ± 0.0008	2.124 ± 0.009	2.17 ± 0.03

Mass Spectrometric Determination of Lead Isotope Ratios by FAB of Glass. In this section the precision and accuracy of the FAB-MS method for measuring lead isotope ratios are compared with the precision and accuracy obtainable by using an isotope ratio instrument. Table II column 1 is a list of the certified NBS values for the lead isotope ratios in the SRM 981 standard "common" lead (29). These results, which represent the external precision of the method, were obtained by the NBS on three different isotope ratio instruments with triple-filament thermal ionization sources and dual detectors.

The glass containing NBS standard 981 "common" lead, whose FAB mass spectrum appears in Figure 1a, was used to study the precision and accuracy with which it is possible to measure lead isotope ratios by FAB-MS. Slow magnetic scanning (0.22 amu/s) over a short range (6 amu) with very fast data accumulation was used to acquire lead isotope ratios. Table II column 2 lists lead isotope ratios obtained by FAB-MS on the glass containing the NBS lead. The mean values in Table II column 2 are for three scans conducted within a period of 10 min and thus represent the internal precision of the method. There were no changes in instrumental conditions during the run. As one can see, the FAB isotope ratio analyses of lead on this instrument are five to ten times less precise than those reported by the NBS under much more stringent experimental conditions.

Table II column 3 lists the isotope ratios of the same NBS lead-containing glass as the mean ratios acquired during six scans taken over the course of several hours during which time the sample probe was removed from the high vacuum between scans, and the FAB gun accelerating voltage and multiplier were turned off between scans. Column 3 shows the external precision of the method and represents much more realistic data-acquisition conditions because the sample probe must be retracted in order to change samples and the high voltages are usually turned off as a safety precaution while the probe is removed. The internal precision and accuracy of the isotope measurements are, as expected, better than the external precision and accuracy.

Clearly, the double-focusing mass spectrometer that was used in this work was not designed to measure isotope ratios precisely; however, the precision was good enough to determine broad distinctions between samples. For example, the precision was good enough to determine whether an artifact was produced in a certain country but not good enough to pinpoint the exact location where the lead in the artifact was mined. There are obviously some experimental errors that make the FAB isotope ratio measurements on the instrumentation used at least an order of magnitude less precise and accurate than the NBS method. Among the sources of inaccuracy and imprecision are probe positioning errors, small changes in voltage due to turning on and off the high-voltage supplies (for the accelerating voltage, FAB gun and electron multiplier), sequential rather than simultaneous detection of isotope intensities, interference from PbH^+ isotopes, and minor isotope discrimination effects of the FAB ionization process.

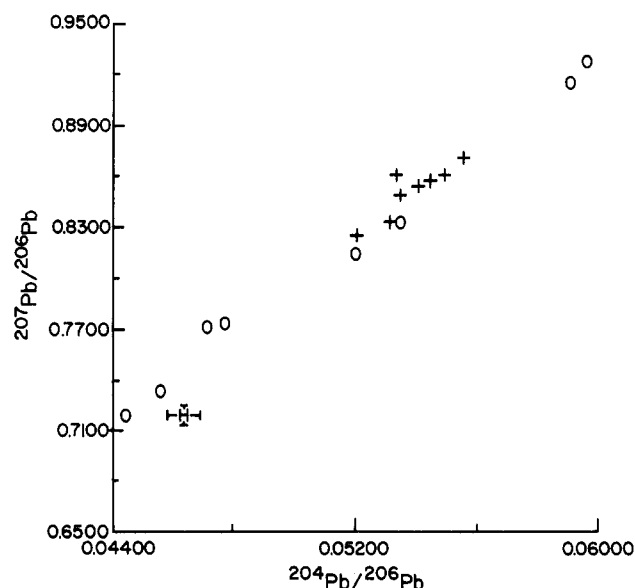


Figure 4. Plot of lead isotope abundance ratio $^{207}Pb/^{206}Pb$ vs. the lead isotope abundance ratio $^{204}Pb/^{206}Pb$ for lead ore samples from England (+) and North America (O) taken from ref 10-12, and for the mean of the Highlands' samples (H). Error bars are given for the determination in our laboratory, and the limits of precision for the other determinations are indicated approximately by the size of the symbol identifying the point.

Possible Origins of the Highlands' Artifacts. Lead isotope ratios from archeological artifacts were obtained by FAB-MS with the realization that only a limited amount of information could be derived from these isotope ratios due to the expected precision of approximately 1% relative standard deviation. From stylistic considerations, the Highlands' ceramics probably either are of British origin or are American copies of British-style pottery (25). Figure 4 is a plot of two sets of lead isotope ratios vs. each other. This method has been used by other researchers to establish reliable geographic distinctions between sets of lead samples (15). The circles (O) indicate lead ores from North America and crosses (+) indicate lead ores from Great Britain. The data were taken from previously published lead isotope ratio studies of lead ores around the world (10-12). Figure 4 shows that lead isotope ratios do not vary much throughout Great Britain and that they do vary enormously in North America. The capital "H" in Figure 4 indicates the average lead isotope ratios for the Highlands' ceramics as obtained by our FAB-MS technique.

It is apparent from Figure 4 that the Highlands' lead isotope ratios fall well outside the range of the British lead ores. This result shows that the ceramics are probably American. Determining the exact origin of the lead in American by using FAB-MS would probably require a multiple collector isotope ratio mass spectrometer.

These experiments suggest that FAB-MS can be used for qualitative determination of inorganic elements and for isotope ratio measurements. By extension of current methodologies and by use of specialized isotope ratio instrumentation, future work on FAB-MS could lead to a quantitative method for inorganic elemental analysis and precise isotope ratio determinations with valuable applications in archaeology.

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Registry No. Lead, 7439-92-1; copper, 7440-50-8; iron, 7439-89-6; aluminum, 7429-90-5; sodium, 7440-23-5; magnesium, 7439-95-4; silicon, 7440-21-3; potassium, 7440-09-7; calcium, 7440-70-2; silica, 7631-86-9; chromium, 7440-47-3; manganese, 7439-96-5.

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Cryogenic Separation of Nitrogen and Oxygen in Air for Determination of Isotopic Ratios by Mass Spectrometry

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A cryogenic separation system has been developed for the quantitative separation of nitrogen and oxygen for high-precision mass spectrometric isotopic determinations. The system is unique in that it does not require conversion of oxygen to CO₂ which allows determination of the ¹⁷O/¹⁶O ratio. Nitrogen and oxygen isotopic ratios obtained are identical with those previously reported for air values.

It is well-known that the precise determination of isotopic ratios is a sensitive and precise diagnostic tool for understanding chemical kinetic, thermodynamic, and physical processes. A recent discovery and documentation of a mass independent isotopic fractionation of oxygen isotopes (¹⁶O, ¹⁷O, and ¹⁸O) in the production of ozone from molecular oxygen suggests that the analysis of the three isotopes of oxygen in atmospheric samples may serve as a unique tracer for stratospheric-tropospheric mixing (1, 2). Theoretical calculations for the photoproduction of ¹⁸O and ¹⁶O atoms from O₂ in the stratosphere (3) also suggest that isotopically characteristic processes may be occurring which are utilizable for tracing events such as atmospheric mixing, ozone-oxygen cycling, and atomic oxygen photoproduction rates. In particular, photochemical processes occurring in the earth's upper atmosphere may result in processes which are mass independent, as reported in laboratory studies (1), whereas tropospheric processes might fractionate the isotopes of oxygen on a mass-

dependent basis. In light of the large atmospheric reservoir of molecular oxygen, the most useful measure will be of the component of smallest magnitude, in this case ¹⁷O (oxygen has natural abundances of 99.758, 0.038, and 0.204 for ¹⁶O, ¹⁷O, and ¹⁸O, respectively). Precise measurements of the isotopes of oxygen are performed by isotope ratio mass spectrometry (4, 5) where, for oxygen, the species measured are ¹⁶O¹⁶O, ¹⁶O¹⁷O, and ¹⁶O¹⁸O (masses 32, 33, 34). In practice, the ratios 34/32 for ¹⁸O/¹⁶O and 33/32 for ¹⁷O/¹⁶O are measured. In order to determine isotopic ratios at an accuracy of 1/10 000, the level required for chemical diagnostic purposes, the sample must be introduced into the mass spectrometer as pure oxygen to avoid isobaric interferences and formation of nitrogen oxides. The ratio of ¹⁸O/¹⁶O is commonly determined mass spectrometrically in the chemical form CO₂ by measuring the 46/44 + 45 mass ratios (4). The drawback to this technique is that ¹⁷O may not be directly determined, because for the species ¹³C¹⁶O¹⁷O, ¹²C¹⁶O¹⁷O, ¹²C¹⁶O¹⁸O, and ¹³C¹⁶O¹⁶O unknown ¹³C/¹²C contributions mask ¹⁷O/¹⁶O variations. A unique and clever technique for ¹⁷O measurement by CO₂ techniques has been described (6), but the procedure requires four mass spectrometric measurements and equilibration with water. The procedure is straightforward, but has the disadvantage that the best precision for ¹⁷O is ±0.5%. We have developed a simple cryogenic procedure which quantitatively separates nitrogen, oxygen, carbon dioxide, and water into individual components allowing isotopic measurements to be performed on each of the species. The