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High-Precision Pb Isotope Analysis by Multicollector-ICP-Mass-Spectrometry Using $^{205}Tl/^{203}Tl$ Normalization: Optimization and Calibration of the Method for the Studies of Pb Isotope Variations

I. V. Chernyshev, A. V. Chugaev, and K. N. Shatagin

Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119017 Russia,

e-mail: chug@igem.ru

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Abstract—The development of the MC-ICP-MS method, which was launched about one decade ago and was largely stimulated by the need to solve geological problems, has opened a new avenue in isotope mass spectrometry. One of the advantages of this method is the possibility of applying a newly developed approach to the correction of analytical results for the effect of mass discrimination by normalizing the measured isotope ratios of an element to a reference (standard) isotope ratio of another element. This makes it possible to overcome the main disadvantage of conventional thermal ionization mass spectrometry (TIMS), in which the effect of mass discrimination cannot be fully taken into account during isotope analysis, and thus to implement a highly accurate method for the analysis of Pb-isotope composition. In application to the capability of the NEPTUNE MC-ICP mass spectrometer, we optimized and calibrated a method for high-accuracy Pb isotope analysis in solutions spiked with Tl, with all currently measured Pb-isotope ratios normalized to the standard $^{205}Tl/^{203}Tl$ ratio (TLN-MC-ICP-MS). The factors affecting the random and systematic analytical errors were examined, and the optimal operating regime and analytical conditions were determined. Much attention was paid to the correlation of the measurement results and the mass discrimination effect determined from the $^{205}Tl/^{203}Tl$ ratio. The value of the $^{205}Tl/^{203}Tl$ normalizing ratio was analytically determined through isotope analyses of the NIST SRM 981, and SRM 982 standard samples of Pb-isotope composition. The data obtained for two mixtures Tl + Pb (SRM 982) and Tl + Pb (SRM 981) in ten replicate analyses were 2.38898 ± 12 and 2.38883 ± 20, respectively. These results are in good mutual agreement, and their general mean $^{205}Tl/^{203}Tl = 2.3889 \pm 1$ coincides (within the error) with the recently published values of 2.3887 ± 7 [Collerson et al., 2002] and 2.3889 ± 1 [Thirlwall, 2002]. The precision of the method (±2SD), which was assayed by the long-term reproducibility of the results of replicate analyses of SRM 981 and seven galena samples (90 analyses) was 0.016–0.018% for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios and 0.005 and 0.009% for the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios, respectively. The precision of the isotope analysis of common Pb was significantly improved (by factors of 6–10 for various isotope ratios) compared with the precision of TIMS techniques acceptable in isotope studies during three decades. The described method was applied to examine the Pb-isotope composition of approximately 250 samples of galena, scheelite, and pyrite from a number of well known (including large) gold, sulfide, and base-metal deposits. The precision of the method (0.01–0.02%) makes it possible to study small inter- and intra-phase differences in Pb-isotope ratios in hydrothermal and magmatic rocks, to assay the scale of regional and variations in the isotope composition of ore Pb, and to correlate the Pb-isotope composition of rocks and ores and reveal its evolutionary trends.

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INTRODUCTION

Isotope studies over the past 20–25 years were conducted at progressively improved sensitivity of Pb-isotope composition determination, which was achieved via developing chemical techniques for the separation of extremely small Pb amounts, a decrease in the total procedural blanks, and, to a much lesser extent, via developing the mass spectrometric isotope analysis itself. The progress in the methods and techniques of multicollector thermal-ionization mass spectrometry (TIMS) that ensured this extremely high accuracy of the measurements of Sr and Nd isotope ratios (up to 0.001–0.0005%) practically did not, however, improve the actual precision of Pb-isotope ratio determination. The typical total errors of the TIMS analysis of common Pb-isotope ratios range from 0.1 to 0.2% depend-

ing on the mass differences of the isotopes. At the same time, it is hard to find a target of isotope studies whose examination does not require a principal improvement of the precision and accuracy of Pb-isotope analysis. Thereby the limitations in the accuracy of isotope analysis are crucial for the studies of geological objects, first of all, ore deposits, which are characterized by relatively narrow (a few fractions of a percent) variations in Pb-isotope ratios.

This publication is devoted to the method of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), which enables the researcher to reach a principally higher level in the precision of the isotope analysis of common Pb.

A little more than ten years has elapsed since the time when the MC-ICP-MS method was designed and applied, first, in a number of pilot models and, then, in several modifications of commercial MC-ICP-MS equipment (manufactured first in the United Kingdom and later in Germany). The development of the MC-ICP-MS method, which opened a new avenue in isotope mass spectrometry, was largely stimulated by the need to solve certain geological problems [1, 2]. Along with geology, this method has found application in nuclear physics, nuclear power engineering, biology, ecology, and other fields, in which the isotope analysis of elements (traditionally conducted by TIMS) was an important part of the research or technology.

The new opportunities opened with the invention of MC-ICP-MS in isotope studies are underlain by the principally important fact that MC-ICP mass spectrometers are able to combine three highly efficient analytical systems: an ion source with ionization in high-temperature plasma, mass analyzer with double focusing ion optics, and multicollector system.

In high-temperature (~8000°C) *plasma*, the nearly complete ionization of atoms of most elements can be achieved, which only weakly depends on the type of the atom and its first ionization potential. *Mass analyzers*, the costliest and most complicated systems of MC-ICP mass spectrometers, can slightly vary in their geometry and design. However, the commonly used combination of an electrostatic analyzer, magnetic sector analyzer, and some additional ionic–optical devises are intended to solve the same problem of multicollector mass spectrometry: to focus the ionic beam into the collectors slits under extremely unfavorable conditions of great energy spread of the ions. At ionization in high-temperature plasma, this scatter is more than one order of magnitude greater that at TIMS and amounts to 25 eV. The design and accuracy of *the multicollector system* in MC-ICP-MS are analogous to those applied in the high-precision (up to 0.0005%) measurements of isotope ratios in the well-known latest TIMS (TRITON and IsoProbe-T).

The mass analyzers of MC-ICP-MS are characterized by approximately one order of magnitude lower ion transmission than in TIMS. Nevertheless, the aforementioned high degree of ionization makes MC-ICP-MS highly advantageous over TIMS in terms of the sensitivity of the isotope analysis of a great number of elements with a high (>7 eV) first ionization potential. Because of this, MC-ICP-MS was lately applied to examine the isotope composition of Fe, Zn, Ag, Ta, B, Hf, and some other elements, which either were previously excluded from the sphere of geochemical research or their study was rather restricted.

Another advantage of the MC-ICP-MS method, which will be considered more closely below, is the possibility of applying a principally new approach to the correction of isotope analysis results for mass discrimination (also referred to as mass bias).

This effect, which is detected on all types of mass spectrometers, including TIMS and various types of ICP-MS, and is related to physical processes in the ion source, in the mass analyzer and collector block of the mass spectrometer, is an important factor worsening the accuracy of isotope analysis for several chemical elements. TIMS development, a process lasting for more than four decades, did not result in a diminution of the integral effect of mass discrimination, and the relative contribution of this effect to the total error of isotope analysis even increased, because the notable decrease in TIMS analytical errors took place at the preservation of the main source of mass discrimination in them: the isotope fractionation of the sample on the filament of the ion source. As a result, the material evaporated from the filament is enriched in lighter isotopes, and the sample is gradually enriched in heavy isotopes in the course of sample depletion. During much of the analysis time span, the directly measured isotope composition of the sample is "lightened" relative to its actual composition.

The two approaches employed in TIMS to correct the measured intensities of the ion currents for mass discrimination involved "internal" and "external" normalization. The former is applied when the element in question contains, along with an isotope of variable abundance (radiogenic isotope), two or more other isotopes with constant ratios of their abundances, which can be utilized as a reference isotope ratio for assaying the mass discrimination effect in the course of isotope analysis. The results are corrected for mass discrimination by normalizing the measured isotope ratios to the reference ratio. As follows from the well-known examples of the application of this approach in geochemical and geochronological research to the isotope analysis of Sr and Nd, this approach makes it possible to almost completely eliminate the mass fractionation effect in analyses on modern TIMS mass spectrometers and, thus, to measure the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios accurate up to 0.001–0.0005%. However, "internal" normalization as a necessary prerequisite of the high accuracy of the analyses is, regretfully, inapplicable to Pb and some other elements whose isotope composition can be of much interest and importance in geology. Three of the four stable Pb isotopes are radiogenic

(^{206}Pb, ^{207}Pb, and ^{208}Pb) and are characterized by more or less variable abundances, and hence, none of the possible isotope ratios of natural Pb can be utilized as a constant one. Because of this, TIMS analyses of Pb are conducted in the overwhelming majority of studies in isotope geochemistry and geochronology with the use of "external" normalization, which is based on determining the integral effect of mass discrimination from the results of independent analyses of standard samples carried out under the same conditions as the analyses of the examined samples. Not going into detail, we only mention that, due to several reasons, "external" normalization does not allow the researcher to completely take into account the mass discrimination effect, which varies from run to run, and thus markedly worsens the precision and accuracy of TIMS isotope analyses. For common Pb, the total error of TIMS isotope ratio determination is approximately 0.05% per mass unit (under ideal conditions, which can be achieved only in the analysis of standard samples), which corresponds to errors of 0.1, 0.15, and 0.2% for the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb ratios, respectively. The analysis of geological samples, particularly those with low Pb concentrations, by TIMS further increases these values.

The sources of mass discrimination in the MC-ICP-MS method will be considered below. Here it is only pertinent to mention that the value of the mass discrimination effect and its variations definitely depend on the design of the mass spectrometers but are controlled mostly by the mass differences of the isotopes of the examined element and are independent (or depend only very insignificantly) of its chemical properties. This provides the possibility of applying "internal" normalization in the MC-ICP-MS method with the normalization of the isotope ratios of the element to be analyzed to the reference isotope ratio of another element. As follows from experience in working on MC-ICP-MS spectrometers [for example, 3, 4, 5], this reference ratio used for Pb analysis can be the ratio of the abundances of the ^{205}Tl and ^{203}Tl isotopes.

The aim of our research (which was conducted on a NEPTUNE MC-ICP-MS) was to develop a method for the highly precise isotope analysis of Pb with the purpose of studying variations in Pb-isotope composition at ore deposits and magmatic rocks, mostly in galena and other minerals (various sulfides, scheelite, and feldspars) with high enough (>10 ppm) Pb concentrations. The problem was proved to be solvable at the standard sensitivity of the equipment, and thus, its sensitivity was not a limiting factor and is not considered in this publication. As is evident from the foregoing, the pivotal problem of the high-precision analysis is the correction of the measurement results for mass discrimination, which is the core issue of this publication.

EXPERIMENTAL DESIGN AND RESULTS

Mass spectrometer

The research was conducted on a NEPTUNE (ThermoFinnigan, Germany) MC-ICP mass spectrometer, which was installed in the Laboratory of Isotope Geochemistry and Geochronology of the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences, in 2003. The mass spectrometer includes a mass analyzer with double ion focusing and ZOOM optics, which enable the direct measuring of isotope ratios with a relative mass difference up to 17%. The accelerating voltage is 10 kV, with the plasma interface under a zero potential. The collector block is equipped with nine Faraday cups and a secondary electron multiplier. The NEPTUNE mass spectrometer is equipped with a Virtual Amplifier system that switches the amplifiers between the Faraday collectors during measurements. This makes it possible to minimize the effect of collector gain uncertainties and improves the overall precision of isotope ratio measurements. The amplifiers have a dynamic range of 50 V.

We used the main variant of isotope multicollector ICP mass spectrometry, which, in fact, makes use of the unique potential of this technique in terms of the precision of isotope analyses for chemical elements: a variant of sample analyzing in the form of solutions. The solutions were injected into the mass spectrometer as aerosol through a quartz spray chamber. The measurements were conducted in low-resolution mode (R ~ 400) to reach the maximum sensitivity of 40 V/μg/ml for ^{208}Pb, which is expressed as the ratio of the intensity of the ^{208}Pb ion beam to the ^{208}Pb concentration in the analyzed solution. The abundance sensitivity, which is conventionally assayed by the mass spectrum of U, was 4×10^{-6}.

The temperature in the room housing the apparatus was maintained constant at 22 ± 2°C with an air conditioning system for preliminary purified air. The water temperature was 20°C for the cooling system of the electric magnet and 16°C for the turbomolecular pumps. The temperature drift of the amplifier unit over the time span of an individual session of measurements did not exceed 0.2°C, which corresponds to variations in the gain factors for less than 0.001%. The major operation parameters of the sample introduction system are listed in Table 1.

In processing and interpreting the results of the mass spectrometric measurements, the following errors were calculated:

(1) the standard error of the mean, which characterizes the convergence of measurements within a given run

$$SE = \sqrt{\frac{\Sigma(x_j - \bar{x})^2}{n(n-1)}},$$

where x_j and $\bar{x}$ are the individual and mean values of isotope ratios in the analysis, and n is the number of measurements within the run;

Table 1. Operation parameters of the NEPTUNE MC-ICP-MS during the isotope analysis of common Pb

Sample Gas flow	0.96 l/min
Cooling Gas flow	17 l/min
Auxiliary Gas flow	1 l/min
Power of RF generator during analysis	950 W
Ion lens voltage	1983 V
Rate of solution injection into the spray chamber	0.4 ml/min
Intensity of the $^{208}Pb^{+}$ ion current	2.5–8 V
Integration time at peaks	8 s
Number of mass spectra per analysis time	27

(2) standard deviation of the measurements, which characterizes the reproducibility of a single analysis in a series of replicate analyses:

$SD = \sqrt{\frac{\Sigma(X_i - \overline{X})^2}{N-1}}$, where X_i and $\overline{X}$ are the individual and average values of isotope ratios in a series of replicate analyses, and N is the number of analyses.

For estimation of precision of the results, we used relative (expressed in %) doubled SE and SD values at a 95% significance level.

Factors Controlling the Precision of Pb Isotope Analysis by MC-ICP-MS

Much attention was focused on examining the factors controlling the random and systematic errors of the analysis: (1) the mass discrimination effect; (2) isobaric interferences at the masses of the analyzed Pb isotopes; (3) the quality of the chemicals used in the analysis; and (4) the effect of the mass spectrometer "memory."

Mass discrimination in ICP mass spectrometers is of a more complicated character than in TIMS instruments and is still poorly explored. It is determined by physical processes in various parts of the mass spectrometer.

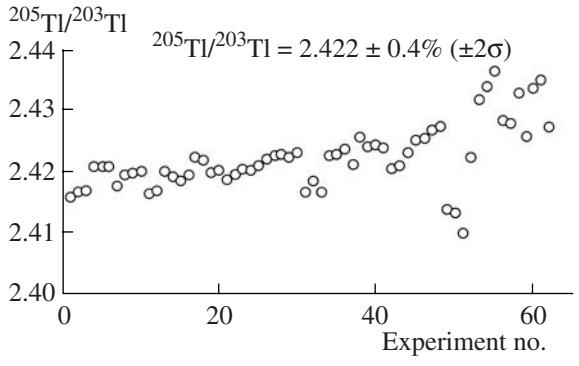

Fig. 1. Reproducibility of the $^{205}Tl/^{203}Tl$ ratio measured in a series of replicate analyses (without correction for mass discrimination).

The authors of the lately published review [6] believe that the processes controlling the mass discrimination effect occur in the plasma torch within the interface, in the ion beam behind the skimmer cone, and in the space of the ion optics. The effect of mass discrimination related to the injection aerosol into the plasma torch is thought to be insignificant compared to other discrimination effects. According to the designers of ICP mass spectrometers at GV Instruments (Manchester, United Kingdom), the effect of mass discrimination is most clearly pronounced in the ICP interface, in the space between the sample cone and skimmer cone from which atoms of the sample are pumped out with the preferable removal of light isotopes (Z. Palacz, personal communication). The isotope composition measured by MC-ICP-MS is heavier that the actual isotope composition of the element, i.e., the mass discrimination effect in mass spectrometers of this type is of opposite sign to TIMS. The integral mass discrimination effect in MC-ICP-MS was evaluated by various researchers at approximately 1% per mass unit for heavy elements and, correspondingly, 25–30% for light isotopes (^{6}Li–^{7}Li and ^{10}B–^{11}B). For comparison, the mass discrimination effect in TIMS is roughly one order of magnitude lower. For example, it amounts to 0.07–0.12% per mass unit for Pb under different analytical conditions.

Observations indicate that the mass discrimination effect depends on several conditions of the analysis, such as the position of the plasma torch relative to the sample cone, the accelerating voltage, the power of the RF generator, the gas flow introducing the sample into the plasma, etc. The complex multifactor character of the mass discrimination phenomenon precludes the quantitative evaluation of the role of each of the factors, but it is possible to quantify the integral effect of mass discrimination in an ICP mass spectrometer and to correspondingly correct the results of the measurements. The solution strategy of this problem is evident from the character of variations in the mass discrimination effect, which can be traced, for example, in the results of Tl and Pb isotope analyses.

Figure 1 shows the $^{205}Tl/^{203}Tl$ ratio measured April 2004 until December 2006. Each point in the plot corresponds to the averaged $^{205}Tl/^{203}Tl$ ratio for an individual run. For the whole set of the analyses, the average $^{205}Tl/^{203}Tl = 2.422$, which is 1.4% higher ("heavier") than the actual value of this ratio, with the scatter of the results of the replicate analyses (expressed as ±2SD) amounting to ±0.4%. The variations in the $^{205}Tl/^{203}Tl$ ratio during each individual run are roughly one order of magnitude lower. A similar scatter and deviations from the true value were also exhibited by the measurements of the $^{208}Pb/^{206}Pb$ ratio, which has a relative mass difference close to that of the $^{205}Tl/^{203}Tl$ ratio (Table 2, left-hand column).

These data typical of the MC-ICP-MS technique obviously imply that any variants of the "external" nor-

malization, when the sample and standard are analyzed in replicate experiments, should not result in any significant improvement of the precision and accuracy of the results (compared to the value of ±0.4%). The accuracy of Pb isotope analysis would be comparable to the values for individual experiments (i.e., 0.1%) and can be achieved only by means of "internal" normalization at simultaneously measured isotope ratios in the sample and standard.

The utilization of the $^{205}Tl/^{203}Tl$ ratio for correction of MC-ICP-MS isotope analyses for the mass discrimination effect is related to the problem of selecting the value for the $^{205}Tl/^{203}Tl$ normalization ratio. The values assumed for this ratio in various publications devoted to this technique slightly varied (Table 3), and it cannot be ruled out that these differences were caused by the fact that the authors of these publications used Tl with different $^{205}Tl/^{203}Tl$ ratios. At least, it was specified only in three of the aforementioned papers [3, 7, 8] that the analyzed Tl was the same: in the NIST SRM 997 standard for the Tl isotope composition. However, the differences in the assumed $^{205}Tl/^{203}Tl$ ratios most probably stem from the individual characteristics of the equipment used for the experiments. The certified $^{205}Tl/^{203}Tl$ ratio for the SRM 997 standard is 2.3871 ± 10 [9]. At the same time, using this standard in the analysis of Pb-isotope composition, the authors of the three publications mentioned above utilized different (2.3869 and 2.3875) values, and both of them were also differed from the certified one. These values were selected empirically and allowed these researchers to make the Pb-isotope ratios measured in the NIST SRM 981 isotope standard consistent with the refined and currently adopted values.

One of the tasks of our research was to analytically determine the value of the $^{205}Tl/^{203}Tl$ normalization ratio. The thallium used in our research was analytical-grade thallium nitride of unknown isotope composition. Its test for a Pb admixture on a NEPTUNE mass spectrometer has shown that, at working ion current of the ^{205}Tl isotope equal to 1×10^{-11} A, the ion currents at the masses of Pb isotopes did not exceed the level of usual background of the mass spectrometer ($< 3 \times 10^{-15}$ A). To determine the $^{205}Tl/^{203}Tl$ ratio, we used the well-known NIST SRM 982 and SRM 981 standards of Pb isotope composition. The selected reference isotope ratio was $^{208}Pb/^{206}Pb$, whose values in the samples were equal to 1.00016 and 2.1677.[1] From the standpoint of the achievable precision and accuracy, the SRM 982 Pb standard is more suitable because of the equity of the ion beams of the 206 and 208 isotopes. In determining the $^{205}Tl/^{203}Tl$ ratio, we used the SRM 981 standard sample as a check. Further, the results of multiple replicate analyses of sample SRM 981 were utilized to assay the long-term precision of the isotope analysis by this method.

[1] U.S.A. National Institute of Standards and Technology, Certificate Analysis SRM 981, SRM 982.

Table 2. Determination of the $^{205}Tl/^{203}Tl$ normalization ratio on a NEPTUNE MC-ICP-MS through the analyses of the Pb SRM 981 and SRM 982 Pb standard samples

Numbers of replicate analyses	Measured $^{208}Pb/^{206}Pb$ ratio ±2SE	Normalized $^{207}Pb/^{206}Pb$ ratio ±2SE	Normalized $^{205}Tl/^{203}Tl$ ratio ±2SE
*Mixture Tl + Pb SRM 982, $^{208}Pb/^{206}Pb$ = 1.00016**			
1	1.01850 ± 6	0.467086 ± 7	2.38885 ± 12
2	1.01860 ± 4	0.467085 ± 5	2.38891 ± 6
3	1.01621 ± 6	0.467087 ± 5	2.38896 ± 6
4	1.01697 ± 9	0.467094 ± 6	2.38909 ± 7
5	1.01694 ± 7	0.467089 ± 3	2.38901 ± 5
6	1.01699 ± 8	0.467091 ± 8	2.38897 ± 6
7	1.01649 ± 14	0.467095 ± 4	2.38903 ± 6
8	1.01675 ± 5	0.467090 ± 8	2.38900 ± 6
9	1.01674 ± 6	0.467085 ± 5	2.38899 ± 5
10	1.01702 ± 6	0.467091 ± 5	2.38898 ± 7
Average	1.0171 ± 16	0.467089 ± 8	2.38898 ± 12
(±2SD)	(±0.16%)	(±0.002%)	(±0.005%)
*Mixture Tl + Pb SRM 981, $^{208}Pb/^{206}Pb$ = 2.1677***			
1	2.19950 ± 30	0.91490 ± 4	2.38874 ± 20
2	2.19992 ± 6	0.91486 ± 2	2.38889 ± 8
3	2.20030 ± 11	0.91494 ± 3	2.38896 ± 12
4	2.20080 ± 8	0.91488 ± 3	2.38887 ± 14
5	2.20128 ± 18	0.91486 ± 2	2.38867 ± 11
6	2.20921 ± 6	0.91487 ± 3	2.38884 ± 15
7	2.20901 ± 15	0.91485 ± 3	2.38874 ± 18
8	2.20965 ± 12	0.91485 ± 2	2.38891 ± 18
9	2.21051 ± 8	0.91486 ± 1	2.38882 ± 14
10	2.20853 ± 18	0.91485 ± 3	2.38889 ± 11
Average	2.205 ± 10	0.91487 ± 6	2.38883 ± 20
(±2SD)	(±0.45%)	(±0.007)	(±0.008%)

Note: Here and below, the reported errors refer to the last significant digits of the corresponding values.

* 3% HNO_3 solution containing 40 ng/ml Tl and 360 ng/ml Pb. Ion current: 1.5×10^{-11} A for $^{205}Tl^+$ and $5–6 \times 10^{-11}$ A for $^{208}Pb^+$.

** 3% HNO_3 solution containing 22 ng/ml Tl and 190 ng/ml Pb. Ion current: 0.6×10^{-11} A for $^{205}Tl^+$ and $3–4 \times 10^{-11}$ A for $^{208}Pb^+$.

Analyzing two prepared mixtures of Tl with each of the aforementioned standards, we solved a problem inverse to that of precise Pb isotope analyses: the measured $^{205}Tl/^{203}Tl$ values were normalized to the assumed values of the $^{208}Pb/^{206}Pb$ ratio. The normalization was

Table 3. Values of the $^{205}Tl/^{203}Tl$ ratio used for correcting Pb isotope analyses for mass discrimination

Reference	MC-ICP-MS model	$^{205}Tl/^{203}Tl$ (±2SD)
Rehkamper, Halliday, 1998	VG Plasma 54	2.3875
Belshaw et al., 1998	Nu-Plasma	2.3875
White et al., 2000	VG Plasma 54	2.3869
Collerson et al., 2002	IsoProbe	2.3887 ± 7
Thirlwall, 2002	IsoProbe	2.3889 ± 1
This publication, 2007	NEPTUNE	2.3889 ± 1

accomplished according to the exponential law. All calculations were carried out using the software of the NEPTUNE mass spectrometer.

Table 2 reports the results of ten individual runs with each of the mixtures: Tl + Pb (SRM 982) and Tl + Pb (SRM 981), and the note to this table specifies the analytical conditions. The results show systematic (~1.7%) differences, caused by the effect of mass discrimination, between the measured values of the reference $^{208}Pb/^{206}Pb$ ratio and the values assumed for both standards. The scatter in the $^{208}Pb/^{206}Pb$ ratios in replicate analyses due to the varying component of the mass discrimination effect is much smaller: ±0.16% (±2SD) according to the results obtained for SRM 982 and ±0.45% (±2SD) for SRM 981. As was demonstrated above (Fig. 1), a similar scatter (±0.4%) characterizes the $^{205}Tl/^{203}Tl$ ratios directly measured in replicate runs. At the same time, Table 2 demonstrates that the $^{205}Tl/^{203}Tl$ ratio normalized to the reference $^{208}Pb/^{206}Pb$ ratio is reproduced from one experiment to another for the mixtures Tl + Pb (SRM 982) and Tl + Pb (SRM 981) with a scatter of ±0.005 and ±0.008% (±2SD), respectively. The average values of the $^{205}Tl/^{203}Tl$ ratio obtained for both mixtures, 2.3890 ± 0.0001 (±2SD) and 2.3888 ± 0.0002 (±2SD), coincide within the error, which allowed us to assume a general average $^{205}Tl/^{203}Tl = 2.3889 \pm 0.0001$ (±2SD) for both series. This ratio was further used as the normalizing (or reference) value to correct the results of Pb-isotope measurements. As can be seen from Table 3, this value is in good agreement with the $^{205}Tl/^{203}Tl$ ratios measured in [4, 5]. An additional criterion of the accuracy of the $^{205}Tl/^{203}Tl$ ratios obtained for the mixtures Tl + Pb (SRM 982) and Tl + Pb (SRM 981) was their measured $^{207}Pb/^{206}Pb$ ratios, which were also (as the $^{205}Tl/^{203}Tl$ ratio) normalized to the reference $^{208}Pb/^{206}Pb$ values (1.00016 and 2.1677). These $^{207}Pb/^{206}Pb$ values are 0.467089 ± 8 and 0.91487 ± 6 for SRM 982 and SRM 981, respectively, and coincide (within the errors) with the refined values presented in [4, 10]. [2]

Isobaric interference is a factor that can significantly affect the precision and accuracy of isotope analyses by the MC-ICP-MS technique. In the analysis of Pb, this factor is the isobaric interference of the $^{204}Hg^+$on the $^{204}Pb^+$, which cannot be eliminated even in high resolution mode. The most efficient method for eliminating this factor is the correction of the intensity of the ion beam at 204 m/e by the intensity of $^{202}Hg^+$, which is registered simultaneously with Pb isotopes. The correction is performed using the ratio of the natural abundances of Hg isotopes $^{202}Hg/^{204}Hg$ for which the value of 4.350 is assumed. Thereby the actual contribution of $^{204}Hg^+$ to the total intensity of the ion beam at 204 m/e does not exceed 4×10^{-17} A. In its correction by the intensity of $^{202}Hg^+$, the contribution of this interference to the total error in the measured $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, and $^{207}Pb/^{204}Pb$ ratios is less than 0.001%.

The role of the purity of the chemicals in the overall balance of factors affecting the precision and accuracy of Pb isotope analyses is high enough. Experiments demonstrate that the contribution of this factor, which is equivalent to a background of 5×10^{-15} A at 208 m/e, can be minimized via the use of chemicals (acids and water) preliminarily purified by subboiling distillation.

Because of some technical features of the method used to introduce the sample into the plasma ion source in the MC-ICP-MS equipment, isotope analysis by this equipment is related to the so-called memory effect. Its minimization involves the purification procedure of the sample introduction system and the continuous control of the background ion currents at the masses of the analyzed isotopes, in our case, from 202 to 208 m/e.

Optimized Method for the Isotope Analysis of Common Pb and Error Estimation

With regard for the results of the experimental study of the aforementioned factors, on a NEPTUNE mass spectrometer we determined the conditions of common Pb isotope analysis. The working parameters of the mass spectrometer are reported in Table 1. We used seven of the nine available Faraday collectors. The ion currents of the 208, 207, 206, and 204 Pb isotopes were measured using the H3, H2, H1, and L1 collectors, whereas $^{205}Tl^+$, $^{203}Tl^+$, and $^{202}Hg^+$ were measured by the Ax, L2, and L3 collectors, respectively (Table 4).

Pb for analysis was dissolved in 3% HNO_3, which was preparatorily doped with Tl (20 ng/ml). The water utilized to prepare 3% HNO_3 was preliminarily purified on an Elix-3 (Millipore, France) devise until acquiring resistance of 15 MΩ cm and was then distilled by subboiling in Teflon vessels (Savillex, United States). Nitric acid (of original reagent-grade purity) was doubly distilled in a quartz apparatus, after which it was

[2] The values of the $^{207}Pb/^{206}Pb$ ratio given in [4, 10] are as follows: (1) TIMS technique with double isotope dilution—0.467038 ± 47 and 0.467063 ± 39 (SRM 982) and 0.91480 ± 9 and 0.91483 ± 6 (SRM 981); (2) MC-ICP-MS technique with internal normalization to the $^{208}Pb/^{207}Pb$ ratio—0.467087 ± 12 (SRM 982) and 0.91489 ± 3 (SRM 981).

Table 4. Positioning of the analyzed peaks in the Multicollector System of the NEPTUNE MC-ICP-MS during the isotope analysis of common Pb

Collector	L3	L2	L1	Ax	H1	H2	H3
Analyzed isotopes	202 Hg	203 Tl	204 Pb	205 Tl	206 Pb	207 Pb	208 Pb
Interference			204 Hg				

additionally distilled by subboiling. In describing the technology for preparing reactants, the 3% HNO_3 working solution was characterized by a satisfactorily low Pb concentration: <10 pg/ml. The Pb concentration in the analyzed solutions of the standard samples, minerals (galena, potassic feldspar, pyrite, and scheelite) and magmatic rocks, was close to 200 ng/ml. The analyses were conducted on 3- to 5-ml of the working solutions.

The amplifiers were calibrated in the beginning of each measurement series. All analyses were performed in static mode. The isotope analysis involved the registration of 27 mass scans at an integration time at peaks equal to 8 s. The baseline of the electrometric amplifiers was measured and peaks were centered in every fourth scan. The intensity of the $^{208}Pb^+$ ion beam usually varied from 2.5×10^{-11} to 8.0×10^{-11} A depending on the Pb concentration in the solution. The background signals did not exceed 3×10^{-15} for $^{208}Pb^+$ and 1.5×10^{-15} A for $^{202}Hg^+$ over the whole time span of the run.

The results of the measurements were processed by the software package of the NEPTUNE mass spectrometer. The measured isotope ratios were normalized to the $^{205}Tl/^{203}Tl = 2.3889$ reference ratio according to the exponential law.

The precision and accuracy of the method were estimated using analyses of the SRM 981 standard that were systematically measured over a long period of time (Table 5) and according to the results of replicate analyses of galena samples (Table 6), which were carried out as checks in the course of studying some ore deposits by the MC-ICP-MS technique. Table 5 presents the results of 62 analyses of the SRM 981 standard sample made between April 2004 and December 2006, along with averages for the five isotope ratios and the precisions of the individual runs (±2SD). The current results obtained during this time period for $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, and $^{207}Pb/^{206}Pb$ are shown in Fig. 2. The errors displayed in the figure for individual analyses correspond to ±2SE.

DISCUSSION

The measure of the precision of isotope analyses used in geochemical studies to assay the differences or similarities between the determined Pb-isotope characteristics of the samples is the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ value 2SD. As can be seen from Table 5, this value for the method described in this publication ranges from 0.016 and 0.018% for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ isotope ratios and 0.005 and 0.009% for $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, respectively. The errors of the former three isotope ratios are closely similar.

The results of replicate Pb analyses in galena samples from various deposits (Table 6) confirmed the conclusion drawn above for the precision of the MC-ICP-MS technique: all differences between the isotope ratios obtained in replicate analyses for a single sample and the corresponding averages do not exceed ±2SD value (%) determined by replicate analyses of the SRM 981 standard (Table 5). Figure 2 and Table 6 also demonstrate that the two standard-error (±2SE) within-run precision (which is shown in graphical and numerical forms) is of the same order of magnitude as the precision of replicate analyses, and thereby always 2SE < 2SD.

The precision of Pb-isotope analysis achieved in our research with the use of the MC-ICP-MS method can be compared with the results obtained by other researchers by the same technique on VG Plasma 54 [8] and Micromass IsoProbe [4, 5, 11] equipment. Their accuracy estimates (±2SD) derived from replicate analyses of the SRM 981 standard notably vary and lie within the following limits: 0.010–0.045% for $^{206}Pb/^{204}Pb$, 0.015–0.025% for $^{207}Pb/^{204}Pb$, 0.017–0.021 for $^{208}Pb/^{204}Pb$, 0.005–0.015% for $^{207}Pb/^{206}Pb$, and

Table 5. Average results of Pb-isotope analysis in the SRM 981 standard sample on a NEPTUNE MC-ICP-MS with the normalization of the results to the $^{205}Tl/^{203}Tl$ ratio. Data of 62 replicate analyses over the time period from April 2005 until December 2006

Isotope ratio	Average value ($N = 62$)	±2SE, % average value	±2SD	±2SD, %
$^{208}Pb/^{204}Pb$	36.7240	±0.011	±0.0060	±0.016
$^{207}Pb/^{204}Pb$	15.4994	±0.010	±0.0025	±0.016
$^{206}Pb/^{204}Pb$	16.9412	±0.0097	±0.0030	±0.018
$^{207}Pb/^{206}Pb$	0.91489	±0.0024	±0.00005	±0.005
$^{208}Pb/^{206}Pb$	2.1677	±0.004	±0.0002	±0.009

Table 6. Reproducibility of the measurement results of the Pb-isotope composition of galena from Ural massive sulfide and base-metal deposits and Western Carpathians, Slovakia, Au–Ag–base-metal deposits obtained in replicate analyses on a NEPTUNE MC-ICP-MS

Deposit	Sample	Data of analysis	$^{206}Pb/^{204}Pb$ (±2SE)	$^{207}Pb/^{204}Pb$ (±2SE)	$^{208}Pb/^{204}Pb$ (±2SE)
Kaban,	У-3423	28.03.06	17.7269 ± 11	15.4910 ± 09	37.5429 ± 30
Ural, Russia		29.03.06	17.7281 ± 11	15.4935 ± 09	37.5511 ± 30
		30.03.06	17.7288 ± 07	15.4938 ± 06	37.5509 ± 23
		Average	17.7279 ± 20	15.4928 ± 30	37.5483 ± 94
Dzhusinskoe,	Т-80/4	23.03.06	18.0979 ± 14	15.6147 ± 12	37.9649 ± 34
Ural, Russia		29.03.06	18.0995 ± 07	15.6130 ± 08	37.9671 ± 23
		30.03.06	18.1005 ± 09	15.6146 ± 08	37.9722 ± 27
		Average	18.0993 ± 26	15.6141 ± 18	37.9681 ± 74
Banska	Te-1-10	29.04.04	18.8230 ± 08	15.6787 ± 07	39.0226 ± 21
Stiavnica,		05.05.04	18.8246 ± 25	15.6801 ± 22	39.0255 ± 56
W. Carpathians,		16.09.04	18.8217 ± 19	15.6775 ± 17	39.0171 ± 50
Slovakia		27.09.04	18.8235 ± 15	15.6798 ± 14	39.0242 ± 40
		Average	18.8232 ± 24	15.6790 ± 24	39.0224 ± 74
Banska	SP-XII-5	16.06.04	18.8206 ± 23	15.6777 ± 16	39.0141 ± 41
Stiavnica,		16.06.04	18.8224 ± 09	15.6791 ± 09	39.0170 ± 27
W. Carpathians,		16.09.04	18.8177 ± 26	15.6752 ± 22	39.0064 ± 55
Slovakia		27.09.04	18.8198 ± 20	15.6780 ± 17	39.0153 ± 46
		Average	18.8201 ± 38	15.6775 ± 32	39.0132 ± 94
Rozalia Mine,	RO-1	16.06.04	18.8833 ± 10	15.6805 ± 09	39.0646 ± 36
Banska Stiavnica,		16.06.04	18.8795 ± 26	15.6782 ± 24	39.0605 ± 58
W. Carpathians,		16.09.04	18.8795 ± 19	15.6771 ± 15	39.0539 ± 40
Slovakia		27.09.04	18.8809 ± 23	15.6792 ± 21	39.0611 ± 54
		Average	18.8808 ± 36	15.6788 ± 29	39.0600 ± 90
Rosalia Mine,	ROZ-XIV-1/91	17.06.04	18.8017 ± 26	15.6808 ± 20	39.0327 ± 46
Banska Stiavnica,		16.09.04	18.8026 ± 27	15.6807 ± 22	39.0293 ± 50
W. Carpathians,		27.09.04	18.8032 ± 24	15.6817 ± 19	39.0336 ± 46
Slovakia		29.09.04	18.7984 ± 23	15.6779 ± 19	39.0229 ± 43
		Average	18.8015 ± 42	15.6803 ± 32	39.0296 ± 98
Brehov,	VSB-6/112	08.09.04	18.9078 ± 23	15.6725 ± 16	38.8938 ± 47
W. Carpathians,		16.09.04	18.9108 ± 19	15.6749 ± 16	38.8984 ± 46
Slovakia		27.09.04	18.9102 ± 24	15.6749 ± 18	38.8993 ± 48
		29.09.04	18.9106 ± 22	15.6748 ± 17	38.8983 ± 42
		Average	18.9099 ± 28	15.6743 ± 24	38.8975 ± 50

0.010–0.033% for $^{208}Pb/^{206}Pb$. As can be readily seen, the errors of our method (Table 5) are close to the minimum values quoted for analogous studies.

The results of the analysis of Pb in SRM 981 also provide insight into the accuracy of the results, because not only the certified values but also the two refined ones for the isotope ratios are currently known for this standard sample. The $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ were refined by M.F. Thirlwall [10], who utilized the method of double isotope dilution: $^{206}Pb/^{204}Pb = 16.9412 \pm 12$ and $^{207}Pb/^{206}Pb = 0.91483 \pm 6$ and 0.91480 ± 9. The results obtained in our work (Table 5) coincide within the error (±2SD) with the values of the corresponding isotope ratios for Pb in SRM 981.

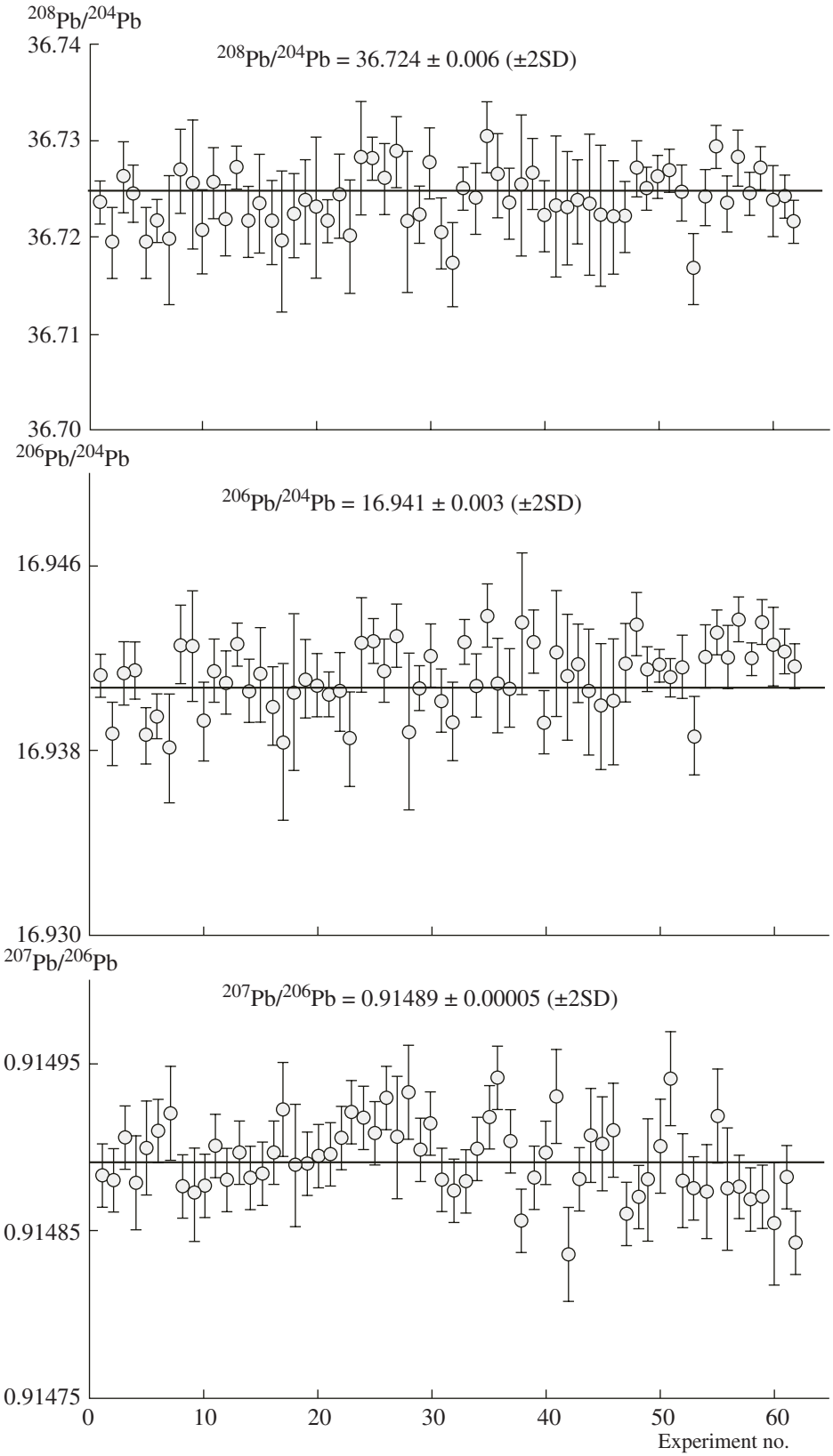

Fig. 2. Reproducibility of the $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, and $^{207}Pb/^{206}Pb$ ratios in a series of replicate analyses of the SRM 981 standard samples obtained on a NEPTUNE MC-ICP-MS with the results normalized to the $^{205}Tl/^{203}Tl$ ratio (see Table 5).

The measurement errors of the $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ ratios are very close (0.016–0.018%), i.e., they do not depend on the mass differences of the isotopes in these ratios. This means that the mass discrimination effects are largely corrected, and the final errors of these three isotope ratios are now affected by other factors, first of all, errors in the measured intensities of the ion currents of the relatively rare ^{204}Pb isotope in these ratios. This follows from the fact that the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios are characterized (Table 5) by much lower errors of 0.005–0.009%. At the same time, these errors are still notably higher than the errors of the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotope ratios, which are measured with the "internal" (in the classic meaning of this term) normalization of the results to the mass discrimination effect. The "residual" error of the Pb-isotope ratios measured by the MC-ICP-MS technique with normalization to the $^{205}Tl/^{203}Tl$ ratio is likely caused by the inexact correspondence between the Pb and Tl mass discrimination coefficients, as was mentioned in [8].

Comparing the sensitivity of the TIMS and MC-ICP-MS techniques, it is pertinent to mention that the Pb amount needed for a single analysis in this variant of the MC-ICP-MS method at this accuracy is equal to 600 ng, whereas the mass of a Pb sample required for TIMS is in the optimal situation 50–100 ng. However, there is a real possibility, first, of at least a threefold decrease in the Pb amount (without decrease in the intensity of the measured ion currents) via the application of an ultrasonic desolvator for sample introduction into the torch. Second, when analyses of small Pb samples should be carried out (for example, in silicate and carbonate rocks and various minerals containing 1–10 ppm Pb), the optimum Pb amount for an MC-ICP-MS analysis can be, for example, two- to fourfold decreased at the sacrifice of an increase in the isotope-ratio measurement error only by a factor of 1.5–2.

As was mentioned above, when developing a MC-ICP-MS technique for high-precision Pb analysis, we were concerned, first of all, with its application in solving various problems related to ore-forming processes. We believe that the MC-ICP-MS technique can not only replace TIMS as a method for common Pb analysis in this field but also will enable obtaining numerous results of principally higher precision and accuracy level, which will provide deeper insight into the reasons for variations in Pb isotope composition. The materials left outside the field of application of the MC-ICP-MS technique will be those with very low (<1 ppm) Pb concentrations.

This method was utilized to study the Pb-isotope composition at some well-known ore deposits, including large ones. We obtained systematic Pb-isotope data on galena from twelve massive sulfide and base-metal deposits in the Ural; gold–silver deposits in the Banska Stiavnica ore field in the Western Carpathians, Slovakia, which are genetically related to Neogene volcanic rocks; and numerous gold deposits in the Verkhoyansk–Kolyma foldbelt, including the Nezhdaninskoe deposit. Moreover, precise Pb isotope analyses were conducted for minerals containing trace amounts of this element: series of samples of pyrite and scheelite from, respectively, the Sukhoi Log deposit in the Baikal–Patom Highland and Kolar in the Kolar greenstone belt in India. The overall number of the samples amounted to approximately 250. These data were partly represented in abstracts and discussed at various conferences [12, 13, 14] and most of them are now prepared for publication. Not touching upon the results of these studies, we would like only to mention here two general conclusions.

The measurements of Pb isotope ratios by the MC-ICP-MS technique accurate to 0.02% make it possible to significantly elucidate the actual scale of these variations in ore Pb. These measurements enabled us to identify some ore deposits or their discrete mineralized zones as those with a homogeneous Pb isotope composition. We were able to reveal differences (or small variations) in the isotope ratios smaller than 0.1%, which are formerly overlapped by the analytical errors of TIMS. The identification of their nature will likely be one of the newly formulated problems of isotope geochemistry.

Another important consequence of the application of the MC-ICP-MS technique is a principal improvement of the analytical reliability of calculated Pb–Pb model ages (T_M). The errors involved in calculated T_M age values the Phanerozoic are at standard analytical errors of Pb-isotope ratios (±0.05% per mass unit), approximately ±35 Ma for TIMS, i.e., is quite significant. The application of the MC-ICP-MS technique reduces this error to ±4 Ma, which makes T_M a sensitive geochemical parameter that can be used as an efficient tool in interpreting results of the isotope analysis of common Pb.

When discussing the new possibilities provided by the application of MC-ICP-MS, it is worth mentioning a number of publications in which the high precision of this technique was employed to identify the source of ore material for Au mineralization [15] and for the solution of such an important problem of isotope geochemistry as determining the trends of Pb isotope ratios and their numerical parameters. Hanano et al. [16] studied volcanic rocks from the Kerguelen Archipelago in the South Indian Ocean by means of precise MC-ICP-MS analysis. The linear trends calculated by these authors in Pb–Pb diagrams testify that the mantle within the Kerguelen plume is heterogeneous. Analyses of Pb in sulfides [5] allowed the authors of this paper to construct an isochron and precisely date the Great Dike in Zimbabwe (at 2578.3 ± 0.9 Ma).

Along with the MC-ICP-MS technique that is discussed in this paper and in which Pb is analyzed in solutions doped with Tl, a variant of the MC-ICP-MS technique was developed in which the sample is obtained

from solid material by means of laser ablation (LA-MC-ICP-MS). At an obvious advantage of this variant (which enables analysis within a spot from 5 to 1000 μm in diameter), it has principal limitations in terms of Pb-isotope analysis.

In the variant with laser ablation, only the "external" normalization can be (and is) used, which results in two additional sources of errors. One of them is related to the fact that the standard and the sample are analyzed in two independent experiments, and the "external" normalization further increases the variable component of the mass discrimination effect of both of them and can be as significant as 0.07–0.4% according to various data. The other source of additional errors is related to the "matrix effect" of the variability of mass discrimination and is underlain by the nonidentity of the standard and samples, namely, their inevitable differences in chemical composition and their chemical and structural heterogeneity. The matrix effect is a source of both random and systematic errors. The method of laser ablation also involves other sources of errors: mass fractionation during the laser evaporation of the sample and the isobaric interferences of polyatomic ions on the masses of Pb isotopes. It is most difficult to reliably measure the ^{204}Pb isotope, which is practically left outside the scope of geochemical consideration when the LA-MC-ICP-MS method is applied because of the low accuracy of this method [17]. Owing to the factors listed above, the possibilities of the calibration of this method and the standardization of analytical errors in LA-MC-ICP-MS, as well as other solid-state analyzers with the use of a laser, are limited.

The errors of the Pb-isotope ratios measured by the MC-ICP-MS technique with laser ablation are much higher than even the errors of TIMS and are one order or more higher than the measurement errors typical of the MC-ICP-MS analyses in solutions. Taking into account that the variations in the Pb isotope composition usually range from a few fractions of a percent to 1–2%, it can be concluded that the advantage of the high spatial resolution of the LA-MC-ICP-MS method is commonly depreciated by its poor analytical precision. Obviously, the application of the LA-MC-ICP-MS technique to Pb isotope studies is limited to the examination of materials with contrasting or even anomalous Pb isotope compositions.

Versions of the MC-ICP-MS technique, a method of precise Pb isotope analysis in solutions, adapted for the analytical characteristics of concrete mass spectrometers were described in a number of papers [4, 5, 8, 11, 12, and this publication] and are based on a common approach: the utilization of the ^{205}Tl/^{203}Tl ratio to correct the mass discrimination effect of Pb isotopes. This leads, however, to terminological confusion concerning the normalizing procedure. Normalization to the ^{205}Tl/^{203}Tl ratio is "external" in the sense that the measured isotope ratios of one element are corrected by the standard isotope ratio of another element. At the same time, this normalization can be regarded as "internal" because (a) all measured isotopes of both elements occur in a single sample (a single analyzed solution), (b) the corrected and correcting isotope ratios are measured strictly synchronously, and (c) the normalization procedure takes into account any variations in the analytical conditions able to affect the mass discrimination effect. The considerations listed above predetermine the result of normalization to the ^{205}Tl/^{203}Tl ratio in the MC-ICP-MS technique and the radical minimization of the effect of mass discrimination on the precision of Pb-isotope composition.

With regard for the aforesaid, the term "internal" normalization seems to be more applicable to this situation. Nevertheless, we believe that, to avoid misunderstanding of the meaning of the technique, none of the terms should be used in its description and, instead, propose the following formulation: **TLN-MC-ICP-MS is a technique for high-precision Pb isotope analysis in solutions doped with Tl, with the normalization of the results of all measured isotope ratios to the standard value of the ^{205}Tl/^{203}Tl ratio**. By analogy with the abbreviated names of other modern techniques of isotope and elemental analyses, the abbreviation TLN-MC-ICP-MS may prove convenient and useful with regard for the ever growing interest in the application of this technique.

CONCLUSIONS

The application of the TLN-MC-ICP-MS technique to Pb isotope analysis makes it possible to largely overcome the major limitation of traditional solid-state mass spectrometry with thermal ionization, namely, the impossibility of introducing complete correction for the mass discrimination of Pb isotopes. This problem can be practically solved by the TLN-MC-ICP-MS technique by means of correcting the measured Pb-isotope ratios to a standard: two Tl isotopes with a mass difference close to that of Pb isotopes. The precision of the isotope analysis of common Pb with the use of this technique is characterized by the following total (±2SD or two sigma) measurement errors of the isotope ratios: ±0.016% for ^{208}Pb/^{204}Pb, ±0.016% for ^{207}Pb/^{204}Pb, ±0.018% for ^{206Pb}/^{204}Pb, ±0.005% for ^{207}Pb/^{206}Pb, and ±0.009% for ^{208}Pb/^{206}Pb. In contrast to the analogous integral estimates for the precision of isotope analysis by TIMS, these values do not exhibit any dependence on the mass difference but are completely determined by the intensities of the ion peaks, i.e., the abundances of the isotopes. The technique described in this paper is less sensitive than TIMS but is characterized by a significantly higher (by factors of 6–10 for various isotope ratios) precision of the isotope analysis for common Pb compared to TIMS and other isotope techniques utilized over the past three decades.

Given the possibility of measuring Pb isotope ratios precise to 0.01–0.02% that can already be provided by the TLN-MC-ICP-MS technique, the most challenging

geochemical problems that can be solved with its help are as follows: the study of small inter- and intraphase differences in isotope ratios at hydrothermal and magmatic rocks, minerals, and ores; the study of regional and local variations in the isotope composition of ore Pb and related genetic reconstructions and predictions; and the correlation of the Pb-isotope composition of rocks and ores with determining the evolutionary trends of these compositions. It is pertinent to add that the territory of Russia, as well as other countries, hosts numerous ore deposits that still have not been subjected to systematic isotope studying due to various reasons. With regard for the reserves of these deposits and their metallogenic and economic importance, many of them can be the subject of the detailed geochemical examination, with the leading role played by the TLN-MC-ICP-MS technique.

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