Chapter

Sequential Speciation Analysis of Metals in Geological Samples by Mass Spectrometry

Jiaquan Xu and Huanwen Chen

Abstract

Sequential analysis of metal speciation in geological samples has been demonstrated using mass spectrometry (MS). Various speciation for metal occurrences, such as water-soluble, exchangeable, oxidable, reducible, and crystalline, have been sequentially extracted from geological samples using a homemade device, followed by online ionized for MS analysis. The metal speciation in geological samples was not only useful for revealing the formation mechanism of geological samples but also beneficial for guiding the separation and exploitation of metals. Compared with the conventional methodology, the present approach takes the advantages of short analysis time (1 h), low sample consumption (1.0 mg), and high recovery (>95%), providing a useful platform for the efficient quantitative speciation analysis of metals in geological samples. This chapter introduces the mechanism and application of the MS approach for the analysis of rare earth minerals, dinosaur fossils, soil, etc.

Keywords: sequential analysis, direct analysis, metal speciation, mass spectrometry, geological samples

1. Introduction

Geological samples include a wide range of substances, such as rocks, minerals, sediments, soil, coal, oil, fossil, atmosphere, and organisms. Chemical analysis of geological samples is one of the primary techniques in earth science, which generally involved to get information on major and trace elements, stable and radioactive isotopes, biomarkers, etc. The distribution coefficients of trace elements have been applied to deduce the diagenetic process [1], while the contents and associations of trace elements are usually employed to discriminate the tectonic environment [2]. Moreover, some trace elements can be regarded as geothermometers and geobarometers to estimate the physical-chemical conditions of diagenesis and mineralization [3]. The fractionation mechanisms of stable isotopes and the decay effects of radioactive isotopes have played an irreplaceable role in solving fundamental problems of earth science [4], by providing valuable information about geological time, terrestrial heat sources, atmosphere-ocean interaction, the evolution of crust and mantle, diagenesis, mineralization, tectonism, paleoclimate, and paleoenvironment. Besides, the speciation of metals also shows great implications for guiding the exploitation of minerals [5]. Overall, chemical analysis of geological samples benefits the understanding of the earth from a microscopic perspective, with diversified application scenarios and broad application prospects.

To date, a great number of approaches have been proposed for the analysis of metal speciation in geological samples, including spectrometry, energy spectrometry, and mass spectrometry. For example, X-ray absorption spectroscopy (XAS) [6], X-ray diffraction (XRD) [7], and X-ray photoelectron spectroscopy (XPS) [8] were both applied to analyze the metal species. The advantages of these methods were that the sample pretreatment was simple and the analytical speed was fast. However, these methods always required a high concentration of metal species because of the relatively low detection sensitivity, and the quantitative performance of these methods was also deficient. On the other side, complex sample pretreatment, such as grinding, digestion, centrifugation, and filtration were used to extract the metal compounds from geological samples. Each process is time-consuming and labor-consuming, and maybe suffer from analytes losses [9]. After the sample pretreatment, the extracted compounds were then analyzed by chromatography methods (e.g., high-performance liquid chromatography, capillary electrophoresis chromatography, etc.) to identify the speciation by retention time, followed by coupling to inductively coupled plasma mass spectrometry (ICP-MS) [10] for quantitative analysis and electrospray ionization (ESI) MS for molecular structure analysis [11], which required expensive instruments and complex operation. Otherwise, a multistep offline sample pretreatment procedure was required for the sequential extraction of different heavy metal fractions according to the association form of metals in the samples [12, 13]. For example, in the Community Bureau of Reference protocol (BCR) method [12], 0.1 mol/L acetic acid (HAC), 0.1 mol/L $NH_2OH{\cdot}HCl$, 8.8 mol/L H_2O_2 and 1.0 mol/L NH_4AC were used sequentially for extraction of different metal speciation from the soil, respectively. Each extraction step took more than 16 h. In the Tessier method [13], 1 mol/L NaAc solution (pH = 8.2), 1 mol/L NaAc/HAc (pH = 5.0), 0.3 mol/L $Na_2S_2O_4$ + 0.2 mol/L Na-citrate +0.03 mol/L $NH_2OH{\cdot}HCl$ in 25% HAC, 0.02 mol/L HNO_3 + 30% H_2O_2 (pH = 2), HF-$HClO_4$ were used to extract exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual fraction or speciation, respectively. The whole procedure would take more than 40 h. The extracted fraction or speciation was then analyzed by ICP-MS [14] or by inductively coupled plasma optical emission spectrometry (ICP-OES) [15]. Thus, a method that has the advantages of without tedious sample pretreatment, high analytical speed, high detection sensitivity, and high accuracy is necessitous for the analysis of the speciation of the metal.

Herein, a new strategy for sequential analysis of metals speciation in geological samples is proposed by regulating the interaction between reagents/energy and geological samples. Assisted by multiple energy forms such as ultrasound and heat, various element species in geological samples were sequentially extracted by chemical reagents with different physicochemical properties of polarity, acidity, and redox using a small amount of samples. The extracted analytes were then ionized online by different ionization techniques (e.g., ESI, ICP, etc.) for MS analysis. This strategy takes the advantages of avoiding sample pretreatment, high analysis speed, low sample consumption, and low labor and energy consumption, which has been used in various areas, such as environment monitoring [16, 17], material science [18, 19], food science [20, 21], life science [22, 23], and geology [24, 25]. In this chapter, we will focus on the application of this sequential speciation analytical strategy in geological samples, such as mineral samples, fossils samples, and soil samples.

2. Sequential speciation analysis of metals in geological samples

2.1 Construction of the sequential ionization device

A sequential ionization device was home-built (**Figure 1**), which consists of eight systems: (1) quantitative addition and mixing system of the chemical reagents, which was used to prepare the corresponding reagents for extraction of the defined speciation from geological samples; (2) microscale liquid sample transportation system, which was used for precision transfer of the reagents and the extracted speciation; (3) microstructure morphology imaging system, which was used to monitor the morphology change in real time; (4) micro-electrolytic cell and interface system, which was used to load the sample; (5) field energy (temperature, ultrasonic, microwave) coupling and regulation system, which was used to promote the extraction of speciation from samples; (6) high-efficiency ionization system, which was used to ionize the extracted speciation; (7) timing trigger and intelligent control system, which was used to control the device; and (8) power supply and support connection system. This device can be directly coupled to the commercial mass spectrometer for direct MS analysis of geological samples.

2.2 Sequential analysis of rare earth elements (REEs) speciation in mineral samples

REEs contained 15 elements of the lanthanide group and yttrium and scandium, which are widely applied in multiple areas, including materials science, energy sources, biomedical science, chemo-catalysis, etc. Rare earth mineral is a kind of non-renewable resource and their reserves are decreasing rapidly. Thus, it is urgent to

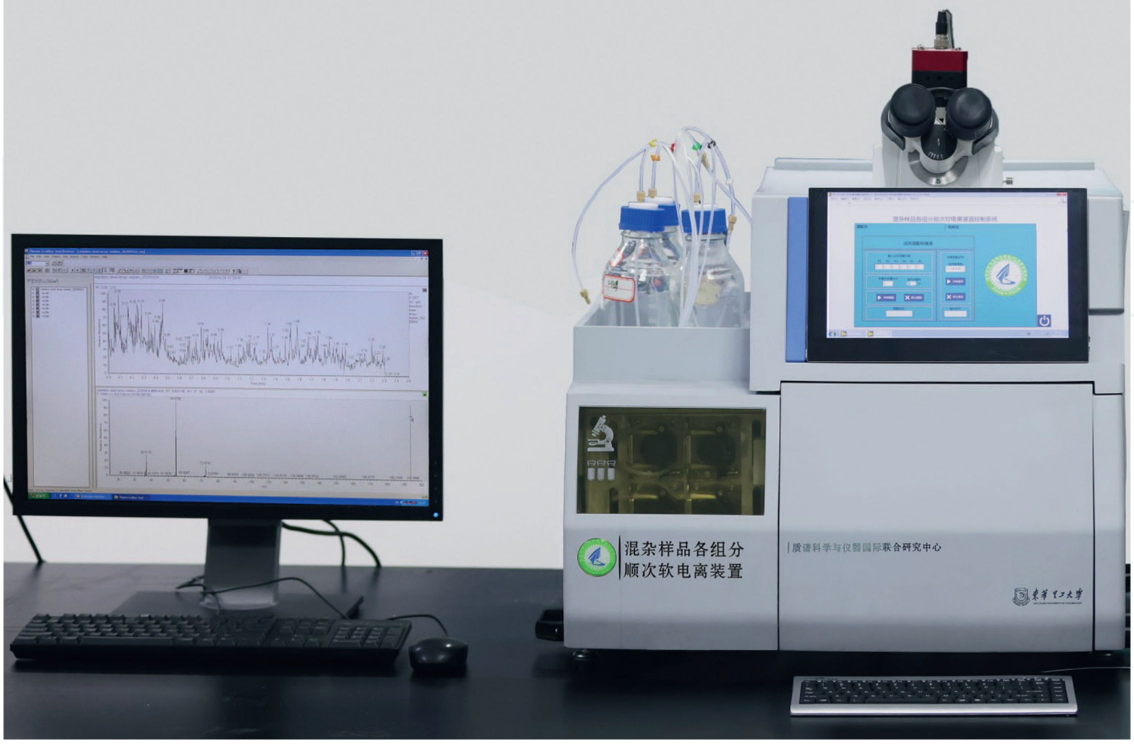

Figure 1.
The picture of a home-built sequential ionization device.

increase the exploration and exploitation efficiency of REEs which is closely related to the elemental speciation of REEs in minerals [5]. For example, ionic rare earth mines are typically exploited by the ion exchange methods [26], while the fluorocarbon cerium earth mines are typically exploited by oxidizing roast chemical methods [27]. Moreover, the information on REEs speciation in mineral samples is useful for the study of metallogenic mechanisms. Therefore, comprehensive analysis of the REEs composition and speciation in mineral samples has great significance for the rare earth industry.

Xu et al. developed a method for rapid characterization of REEs speciation in ore samples by coupling sequential speciation extraction with ICP-MS analysis [24]. As shown in **Figure 2**, six extraction solutions including ① H_2O, ② NH_4AC, ③ NH_2OH-HCl, ④ mixture of HNO_3 and H_2O_2, ⑤ HF, and ⑥ HNO_3 sequentially flowed through the sample chamber at 0.3 mL/min to extract the ① water-soluble REEs speciation, ② exchangeable REEs speciation, ③ reducible REEs speciation, ④ oxidable REEs speciation, and ⑤-⑥crystalline REEs speciation from the REEs ore sample. The extracted REEs species were mixed online with 4% HNO_3 (0.3 mL/min) at the outlet of the sample chamber for online ICP-MS analysis. The extracted ion chromatography (EIC) signals of Y (*m/z* = 89), La (*m/z* = 139), Ce (*m/z* = 140), Pr (*m/z* = 141), Nd (*m/z* = 146), Sm (*m/z* = 147), Eu (*m/z* = 153), Gd (*m/z* = 157), Tb (*m/z* = 159), Dy (*m/z* = 163), Ho (*m/z* = 165), Er (*m/z* = 166), Tm (*m/z* = 169), Yb (*m/z* = 172), and Lu (*m/z* = 175) were recorded in real-time. The extraction solution changed when one speciation MS signal decreased to baseline.

As shown in **Figure 3**, REEs and associated metals (e.g., Mn, Fe, etc.) with five types of speciation, were sequentially detected within 1 h. Standard curves of REEs (**Figure 4a**) and the EIC area of the corresponding REE MS signal (**Figure 3a-o**) were used to quantify the REEs content. The amount of each REE was La 391.7 μg/g, Ce 203.1 μg/g, Pr 74.1 μg/g, Nd 243.9 μg/g, Sm 41.0 μg/g, Eu 5.2 μg/g, Gd 45.9 μg/g, Tb 6.3 μg/g, Dy 28.6 μg/g, Ho 5.5 μg/g, Er 14.9 μg/g, Tm 2.1 μg/g, Yb 10.8 μg/g, Lu 2.0 μg/g, and Y 148.4 μg/g. **Figure 4b** showed the normalized ratio of each REE with the order of La (32.01%) > Nd (19.94%) > Ce (16.60%) > Y (12.13%) > Pr (6.05%) > Gd (3.76%) > Sm (3.35%) > Dy (2.33%) > Er (1.22%) > Yb (0.88%) > Tb (0.52%) > Ho (0.45%) > Eu (0.42%) > Tm (0.17%) > Lu (0.16%). The ratio of

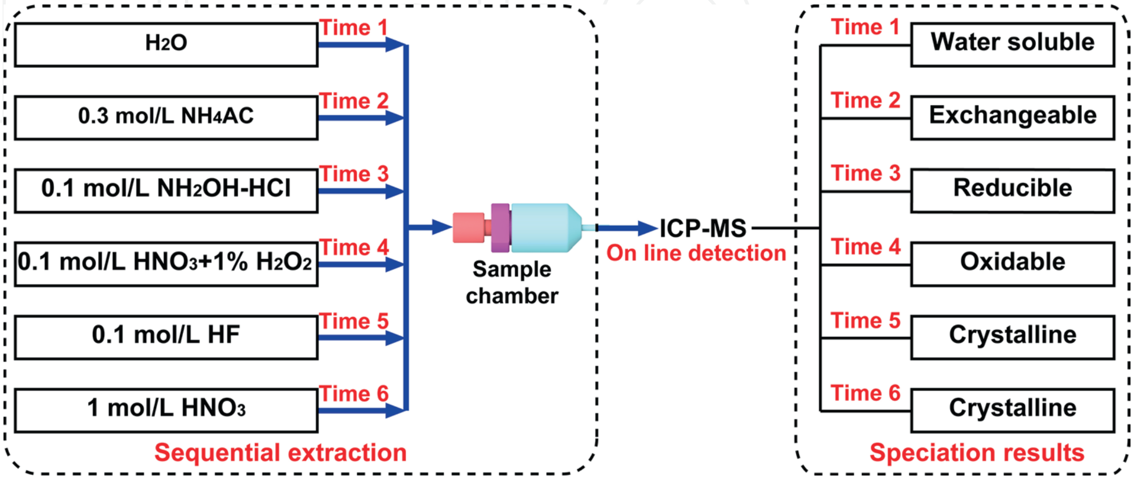

Figure 2.
The procedure for speciation analysis of REEs in ore samples.

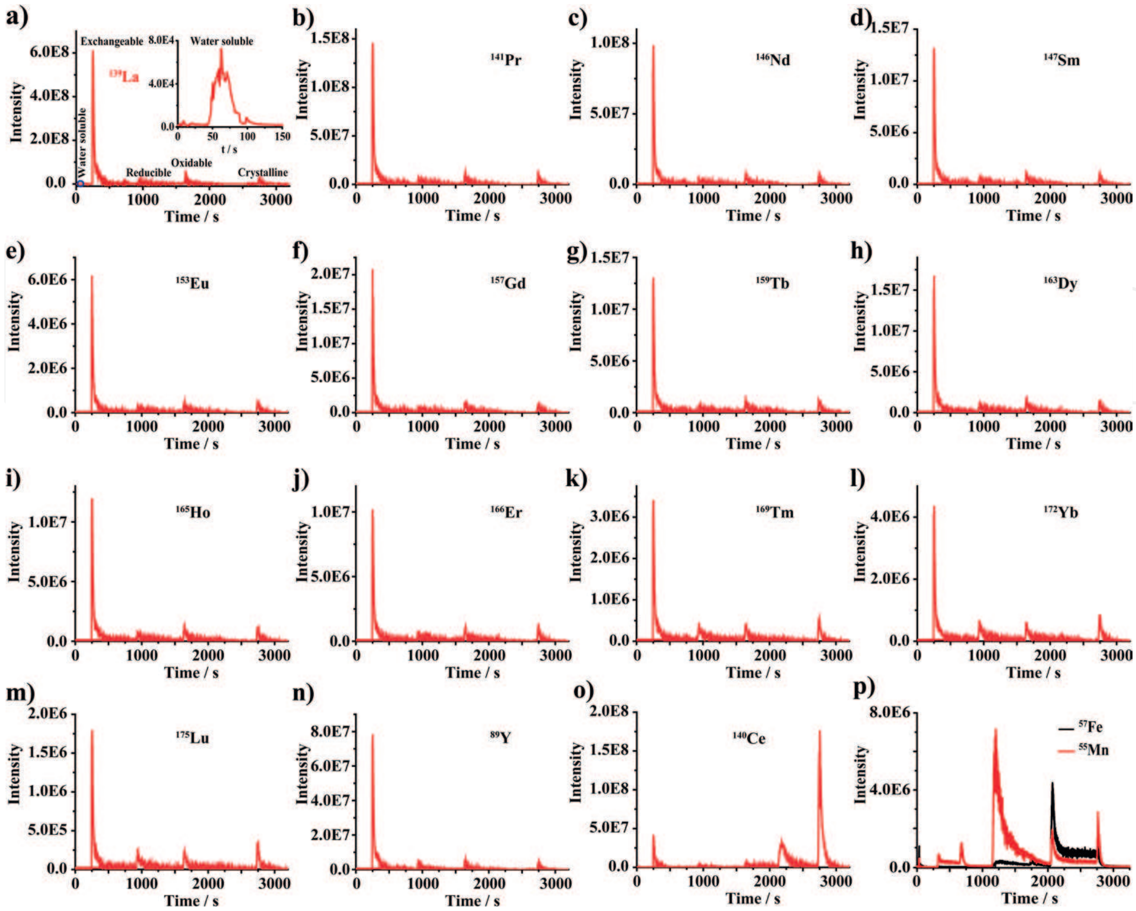

Figure 3.
Analytical results of REEs in an ore sample. a)-o) EIC of 15 kinds of REEs and p) 2 kinds of associated metal elements.

different REEs speciation was shown in **Figure 4c**. For most of the REEs, the exchangeable speciation (>50%) was dominant. However, for Ce, the dominant speciation was the crystalline (≥80%). These results provided essential information for guiding REEs exploration and exploitation.

The quantitative performance of this method was verified by standard methods (**Figure 4d**). The recoveries of most REEs (e.g., La, Ce, Pr, and Nd) were in the range of 95%–110%. However, higher recovery (>120–228%) was observed for those low abundance REEs, such as Er (14.9 μg/g), Yb (10.8 μg/g), Tb (6.3 μg/g), Eu (5.2 μg/g), Tm (2.1 μg/g), and Lu (2.01 μg/g), which could be due to the fact that this method required no sample pretreatment, thus reduced the potential analytes losses which may occur in the conventional methods.

In summary, the sequential speciation analytical method developed by Xu et al. takes the advantage of high analysis speed, high detection throughput, high efficiency, low energy consumption, and low sample consumption. For instance, the sequential speciation analytical method can obtain quantitative results of 15 REEs with five speciations (15*6 = 90 data sets) using 1.0 mg ore sample within an analytical procedure (1 h), which took about 40 s for one data set. In general, the BCR method required about 80 h to get 90 data sets using 1.0 g sample [12], and the Tessier method required about 40 h to get 90 data sets using 1.0 g sample [13]. Besides, no sample pretreatment could greatly lower labor and energy consumption.

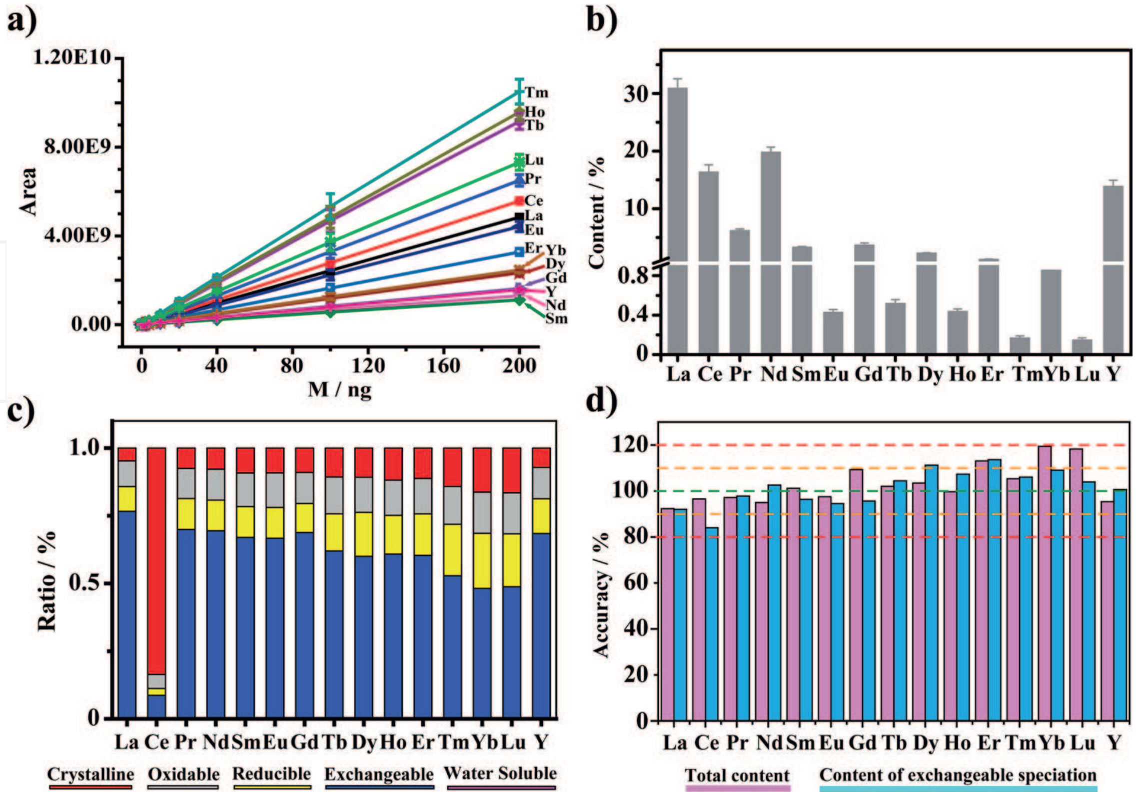

Figure 4.
Quantitative information of REEs speciation in an ore sample. (a) The standard curves of REEs (n = 3); (b) The normalized ratio of REEs; (c) The ratio of REEs speciation; (d) The accuracy of the present method varied by standard methods.

2.3 Sequential analysis of REEs speciation in fossil samples

REEs pattern in fossil samples is useful for taphonomy, provenance, and paleoenvironment [28]. It has been applied to solve some significant problems such as to identify reworked fossil samples as well as a useful indicator of bone provenance within mixed deposits [29]. Besides, the REEs pattern of fossils was also applied for the determination of stratigraphy, such as the dating formation [30]. Basically, REEs enriched in fossils were attributed to a post-mortem process [28]. Two processes were proposed during the enrichment process of REEs, which are substitution and adsorption. These two main processes corporately determined the concentration of REEs in biogenic apatite. On one side, the adsorption process can rapidly reach an equilibrium. However, because of the weak physical molecular force, such as the van der Waals force, these REEs ions can be desorbed easily. On the other side, the substitution process is up to the properties of bulk crystal-chemical, which accounts for the major contribution of concentrated REEs. Therefore, REEs speciation is vitally essential for the research of fossil bones.

Thus, Wang et al. carried out the sequential ionization MS analysis (**Figure 2**) for the quantification of REEs in dinosaur bone fossils samples [25]. Fossil particle samples were sampled in different spots on the horizontal part of the bone fossil. Drilled fossils were ground and filtered to obtain powders using a 200-mesh sieve, followed by a sequential ionization MS procedure as shown in **Figure 2**. As an example, **Figure 5** showed the results of La in a powder sample and particle sample. H_2O was first selected as an eluent to extract the water-soluble REEs. After the MS signal of water-soluble REEs (inset enlarged peaks 1) decreased to zero, 0.3 mol/L NH_4Ac, 0.1 mol/L $NH_2OH{\cdot}HCl$, and a mixture of 0.1 mol/L HNO_3 + 1% H_2O_2, were sequentially

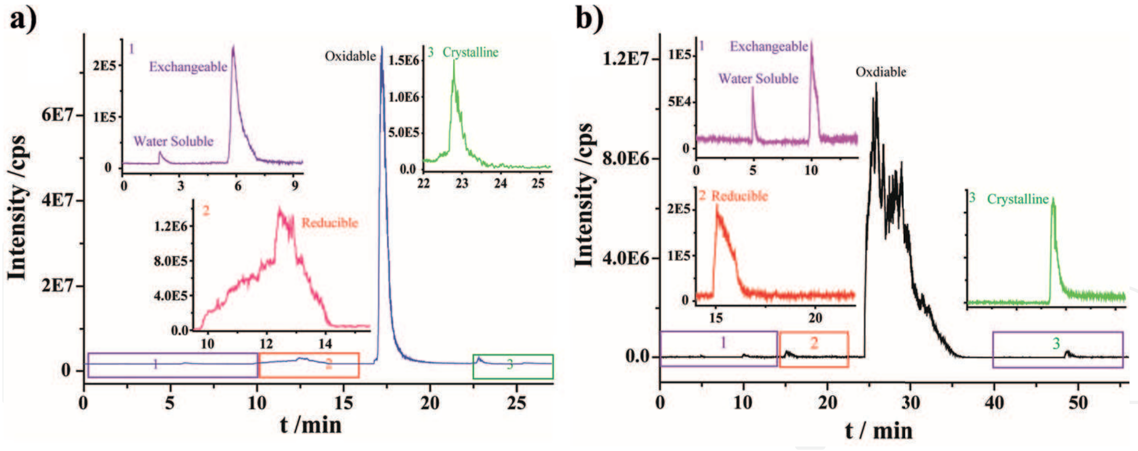

Figure 5.
Sequential analysis of REEs speciation in a dinosaur bone fossil sample. (a) EIC of La in fossil powder; (b) EIC of La in fossil particle. The insets in (a) and (b) were the enlarged REEs peaks.

flowed through the fossil sample to extract the exchangeable REEs, reducible REEs, and oxidable REEs until the MS signals of the previous speciation disappeared. Finally, the crystalline REEs was extracted by 0.1 mol/L HF and 1 mol/L HNO_3 solutions (inset enlarged peaks 3). The contents of REEs speciation were obtained by integrating the EIC area of the REEs speciation peaks and the corresponding standard curve. Compared with traditional standard digestion methods, this method gave similar results of REEs concentration in a dinosaur bone, but with the advantages of a higher analysis speed (1 h), lower sample consumption (1 mg), and more information on spatial distribution. Furthermore, the REEs in both powder samples and particle samples of dinosaur bone could be sequentially detected with high sensitivity in this work. This approach may offer us a wonderful tool for the investigation of REEs distribution in the microstructure of the fossil sample in the future.

2.4 Sequential speciation analysis of heavy metals in soil samples

Heavy metal is one of the most toxic species which exists widely in soil and is closely related to human health [31]. The heavy metals in soil can further enter drink water and plants, and then enter the human body by diet. In particular, the biotoxicity of heavy metals is closely related to their speciation [32]. For example, soluble Pb speciation are easily metastasis and assimilated by the plants, resulting in strong toxicity, while insoluble speciation Pb has weak toxicity. Thus, chemical profiling of heavy metal speciation in soil samples is of great significance for the evaluation of health risks. In addition, the information regarding heavy metal speciation is useful for tracing the pollution source.

Song et al. developed a sequential ionization MS method for analysis of the speciation of the metal in soil samples without sample pretreatment by a combination of a flow electrolytic cell to ESI-MS [17]. Four speciations of heavy metals, including water-soluble speciation, organic speciation, insoluble speciation, and elemental speciation, were extracted sequentially online by H_2O, CH_3OH, EDTA-2Na, and electrolysis for ESI-MS detection. **Figure 6a** displays the high-resolution MS results of $Pb(NO_3)_2$ which was employed as a representative of water-soluble metal compounds. EDTA-2Na was used to chelate the extracted Pb^{2+} online for ESI-MS analysis. The related signals were assigned to $[EDTA\text{-}2H]^{2-}$ (m/z = 145.0370), $[Pb^{206} + EDTA\text{-}4H]^{2-}$ (m/z = 247.0161), $[Pb^{207} + EDTA\text{–}4H]^{2-}$ (m/z = 247.5168),

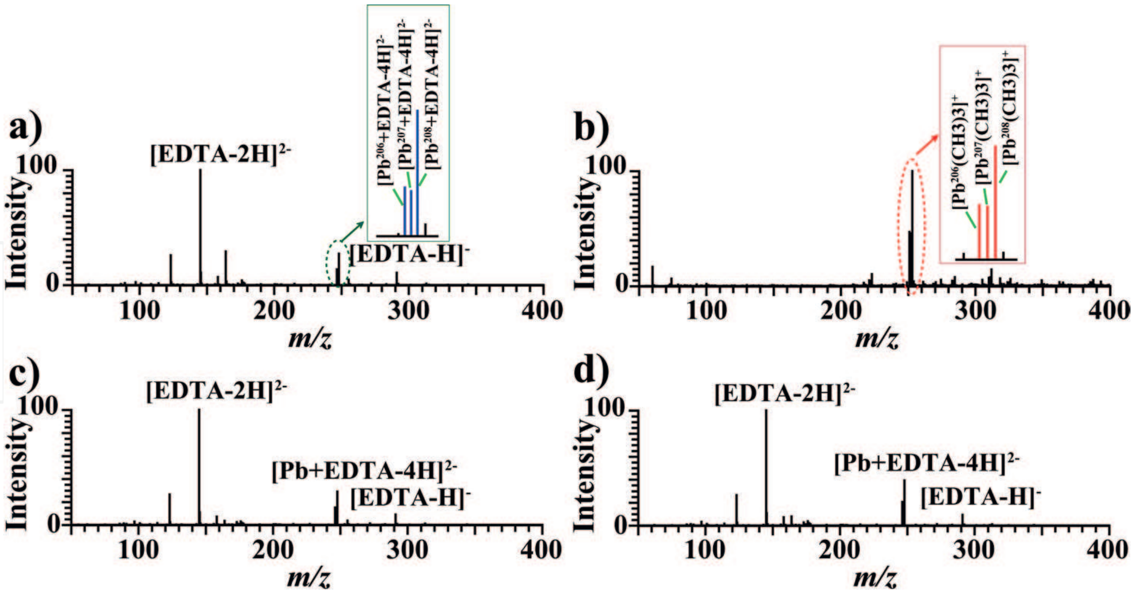

Figure 6.
Qualitative analysis of different speciation Pb by EC-MS. (a) water-soluble speciation $Pb(NO_3)_2$*; (b) organic speciation trimethyl lead chloride; (c) insoluble speciation* $Pb(CO_3)_2$*; (d) elemental Pb.*

$[Pb^{208} + EDTA\text{-}4H]^{2-}$ (m/z = 248.0171) and $[EDTA–H]^{-}$ (m/z = 291.08230) according to the ratio of isotope and high-resolution m/z values. **Figure 6b** displays the MS results of trimethyl lead chloride which was employed as an organic metal compound. Obvious $[Pb^{206}(CH_3)_3]^{+}$ (m/z = 251.0443), $[Pb^{207}(CH_3)_3]^{+}$ (m/z = 252.0458), $[Pb^{208}(CH_3)_3]^{+}$ (m/z = 253.0465) were detected. Because EDTA can form a highly stable complex with most of the metal ions, EDTA-2Na was used as an extraction solution to dissolve the insoluble $PbCO_3$ for MS detection, and obvious $[EDTA\text{-}2H]^{2-}$ (m/z = 145.0370), $[Pb^{206} + EDTA\text{-}4H]^{2-}$ (m/z = 247.0161), $[Pb^{207} + EDTA–4H]^{2-}$ (m/z = 247.5168), $[Pb^{208} + EDTA\text{-}4H]^{2-}$ (m/z = 248.0171), and $[EDTA–H]^{-}$ (m/z = 291.0823) were detected in **Figure 6c**, indicating that using EDTA-2Na to dissolve the insoluble speciation was feasible. Elemental Pb cannot be dissolved by H_2O, CH_3OH, or EDTA-2Na. Strong inorganic acids (e.g., HCl, HNO_3) are typically used for the dissolution of Pb. However, strong inorganic acids would suppress the MS signals and damage the MS instrument. Therefore, the electrolysis method was applied to mildly convert the Pb into Pb^{2+}, followed by reacting with EDTA-2Na in situ to form the EDTA-Pb complex for MS detection. As shown in **Figure 6d**, obvious signals of $[Pb + EDTA–4H]^{2-}$ were also detected.

Figure 7 showed the results of the heavy metals in the faucet sediment obtained by sequential speciation analysis. The whole analytical procedure was completed within 20 min without complex sample pretreatment. The signals of water-soluble speciation, organic speciation, insoluble speciation, and elemental speciation were sequentially detected at 0–4 min, 4–6 min, 6–11 min, and 12–18 min, respectively. The results indicated that the sediment contained water-soluble, insoluble, and elemental Pb, Ni, Zn, and Fe, insoluble and elemental Cu, water-soluble and insoluble Ca, and insoluble Mn. No organic speciation metal was detected in the sediment.

2.5 Sequential speciation analysis of arsenic in sediments and organisms

Despite great efforts have been made to study redox-sensitive elements in the environment such as arsenic (As) and antimony (Sb), there are still some challenges and difficulties

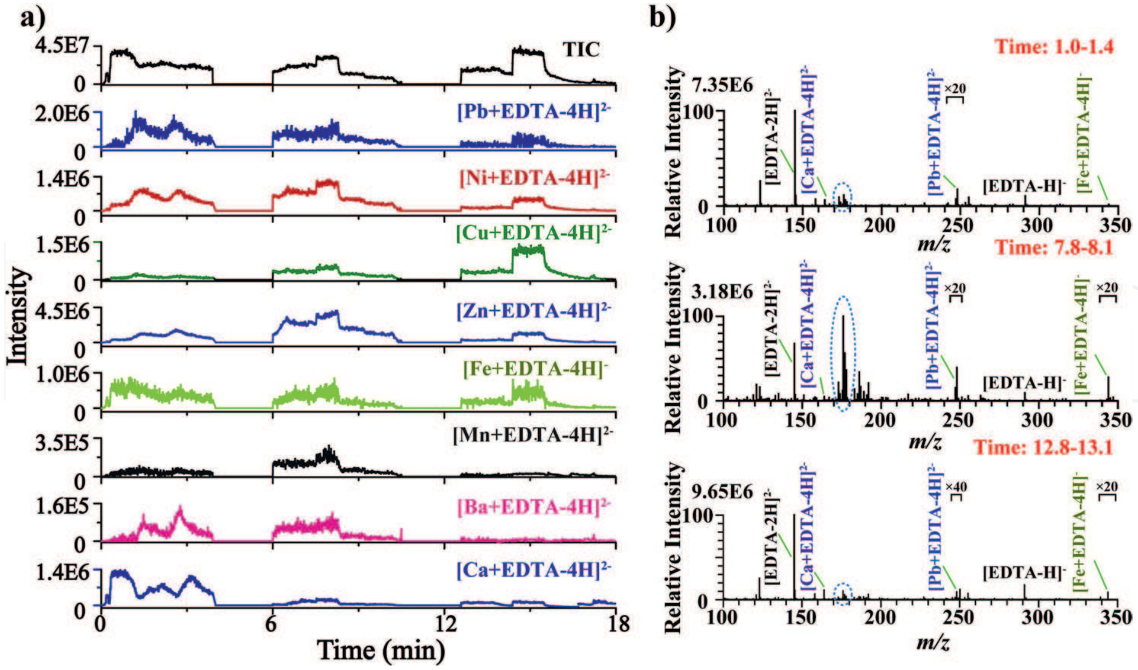

Figure 7.
Application of EC-MS in the analysis of heavy metals in the faucet sediment. (a) EIC of the different speciation of heavy metals; (b) mass spectrum of the corresponding speciation.

for the speciation analysis. As is one of the most toxic elements and exists widely in the natural environment [33]. Furthermore, the chemical behavior of As, such as adsorption, toxicity, transformation, and bioavailability, was not only related to its speciation but also related to the co-existing elements (e.g., Fe, Mn) [34]. Therefore, a robust analytical method is required that can provide information on the concentration, spatial distribution, redox states, and the inter-influence with coexisting elements. However, conventional speciation analysis methods normally required tedious sample pretreatment [12, 13].

Thus, Wu et al. proposed an online sequential fractionation analysis method for As in ferrihydrite samples [16]. As adsorption experiment was first conducted in solution with synthesized ferrihydrites as adsorbents. The collected As-adsorbed ferrihydrite was then used as a raw sample for direct MS analysis. The online fractionation analysis method consisted of eluents, an online extraction device, online acidification, and detection (**Figure 8**). Based on the association between As and iron oxides, various eluents were selected, such as H_2O, 5% NH_4NO_3, 0.2 mol/L $NH_4H_2PO_4$, 0.1 mol/L $(NH_4)_2C_2O_4$ (pH = 3), and a mixture of 0.5% HF and 5% HNO_3, respectively. Online extraction of As, which was assisted by an ultrasonic bath, was then performed and acidified by 2% HNO_3. Finally, the analytes were efficiently detected by ICP-MS.

The results showed that water-soluble fraction, non-specifically adsorbed fraction, specifically adsorbed fraction, iron oxide bonded fraction, and residual fraction were sequentially determined with different proportions (**Figure 9**). For instance, iron oxide bonded As species (83%) and specifically adsorbed As species (13%) were the dominant As(III) fractions on ferrihydrite. The method had the advantages of no sample pretreatment, low sample consumption, high detection sensitivity, short analysis time, and simple experimental manipulation, providing a useful tool for understanding As behavior in the environment. Besides, compared to conventional methods, the present method could provide more information on the As association with iron oxides on the surface of solid samples.

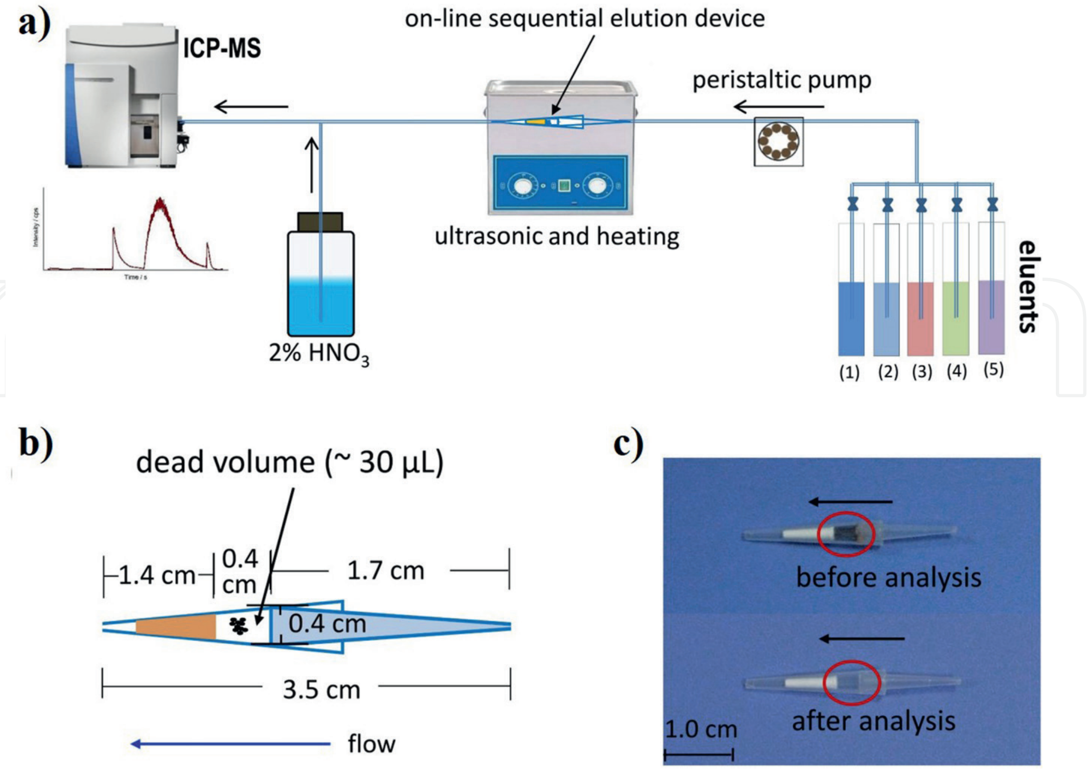

Figure 8.
Sequential analysis of As speciation in ferrihydrite sample. (a) Schematic diagram of online sequential analysis of As species on ferrihydrite. The eluents (1)–(5) are H_2O, 5% NH_4NO_3, 0.2 mol/L $NH_4H_2PO_4$, 0.1 mol/L $(NH_4)_2C_2O_4$ and a mixture of 0.5% HF and 5% HNO_3, respectively; (b) online elution component with detailed parameter; (c) the picture of the sample before and after analysis.

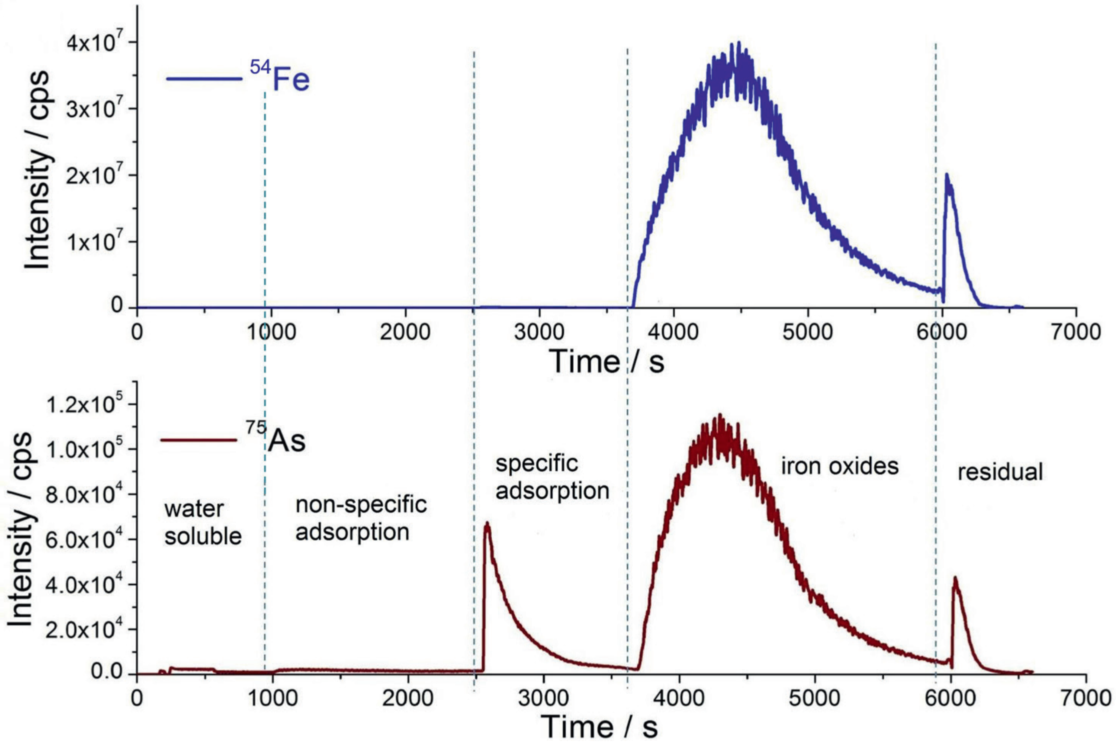

Figure 9.
Sequential analysis of ^{75}As(III) and ^{54}Fe in ferrihydrite.

In the second work, an extraction electrospray ionization-hydride generation-microwave plasma torch-mass spectrometry (EESI-HG-MPT-MS) method was proposed by Wu et al. for online speciation analysis of As from raw bio-matrices [20]. In this work, the MPT was coupled to an organic mass spectrometer for sensitive detection of inorganic arsenic species. The overall setup was mainly composed of five parts, which are detailed in **Figure 10**. A mixture of $CH_3OH/H_2O/HAc$ (V:V:V = 50:49:1) was used as an eluent reagent. Raw samples were extracted online by a syringe pump and an applied high voltage of 4 kV. The As-containing effluent was then either directly ionized for organic As detection or for the detection of inorganic As converted into volatile arsenic hydrides under certain pH conditions. It is worth noting that, in this work, a novel sample introduction device that can be used for both gas and solution samples was prepared by inserting a glass pipette into a larger quartz tube (i.d. 0.25 cm). When the analytes reached the tip of the inner glass pipette, a stable electrospray plume was formed, and therefore organic As could be analyzed directly.

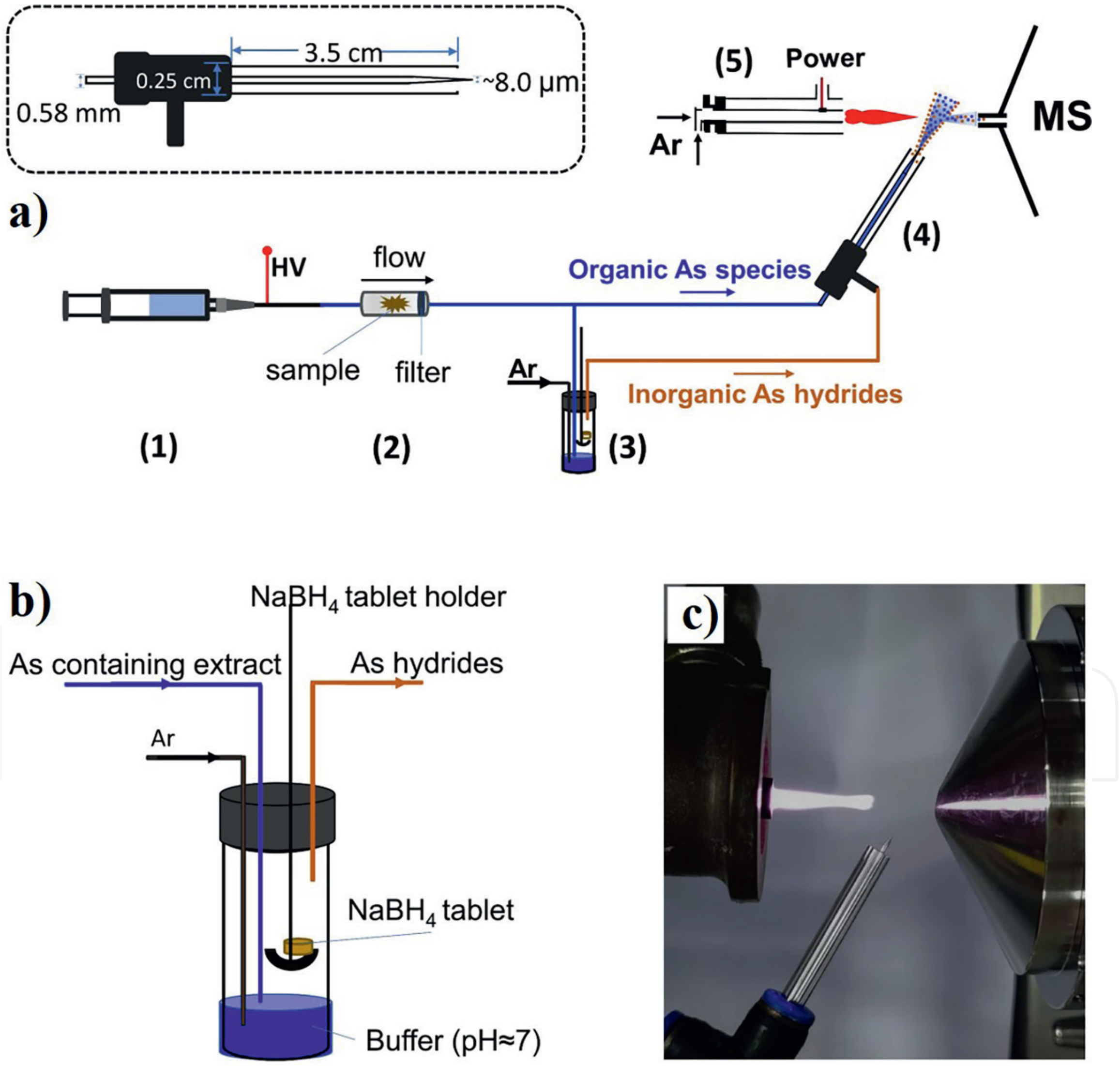

Figure 10.
Sequential analysis of organic and inorganic arsenic species. (a) Schematic diagram of the EESI-HG-MPT-MS, which consists of a (1) syringe pump, (2) sample chamber, (3) generator of hydride As, (4) sample introduction device, (5) MPT and mass spectrometer; (b) schematic diagram of the generator of hydride As; (c) picture of the home-made ion source.

On the other hand, inorganic As was determined via ionization by MPT in the form of m/z 204 ($H_3AsO_4 + NO_3^-$). This method enabled direct obtaining of As speciation in raw biological samples, which avoided multistep extraction and sample preservation, therefore potential redox processes, interconversion, or mass loss could be effectively alleviated. Ambient ionization by MPT allows sensitive detection of inorganic As on a common organic mass spectrometer. The developed method may play a role in different fields such as analytical chemistry, environmental chemistry, and bioanalysis.

3. Conclusions and Future Directions

3.1 Conclusions

In summary, a novel strategy for direct MS analysis of metal speciation in geological samples was proposed by regulating the interaction process between reagents/energy and geological samples, and a sequential ionization device was home-built which can be directly coupled to the commercial mass spectrometer (e.g., ICP-MS, ESI-MS) for the direct MS analysis of geological samples. Rapid sequential characterization of metal speciation in multiple geological samples, such as minerals, fossils, soil, and bio-tissue has been quantitatively achieved based on the sequential analytical strategy and ionization device, without complex sample pretreatment. Compared with traditional methods (e.g., BCR method, Tessier method), the present method offers significant advantages such as high analysis speed, low sample consumption, high recovery, simple operation, low energy and labor consumption, and rich chemical information. These results demonstrate the power of the present method for obtaining information on element abundance, occurrence, and paragenetic association, which is vitally essential for geochemistry.

3.2 Future directions

3.2.1 Sequential analysis of the distribution of metallic constituents in geological samples

Micro-area analysis of geological samples, such as minerals, can provide information on the concentration and distribution of the elements, which is essential for studying the metallogenic mechanism and understanding the structure. In general, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [35], second ion mass spectroscopy (SIMS) [36], proton-induced X-ray emission spectroscopy (PIXRES) [37], etc. were widely used in the micro-area analysis of minerals with point-by-point scanning, which has the advantage of high spatial resolution and disadvantage of time-consuming. Thus, a novel analytical strategy for rapid micro-area analysis is needed. For instance, using a sequential ionization device (**Figure 1**) coupled with MS, the speciation (S) and concentration (C) of the metal in the geological samples can be obtained sequentially with time (T) by MS to establish the relationship Y(S, C) = F(T). Meanwhile, the Microstructure morphology imaging system in the sequential ionization device can record the change of morphology (M) in real time to establish the relationship Y(M) = F(T). By combining the relations the Y(S, C) = F(T) and Y(M) = F(T), a relationship between (S, C) and (M) could be established as Y(S, C) = F(M), which would be the distribution of metal speciation.

3.2.2 Sequential analysis of metallic and organic constituents in geological samples

Besides metallic constituents, organic constituents are also important for geological samples [38]. For example, biomarkers, such as alkanes, aromatic hydrocarbons, terpenoids, steroids, fatty acids, porphyrins, and so on, are helpful in identifying the source of organic matters, inferring the redox conditions of depositional and early diagenetic stages, and in reflecting thermal maturity of sediments. Thus, a method is urgent that could simultaneously analyze the metallic and organic constituents, which would not only provide information on metallic and organic constituents but could also establish the relationship between the metallic and organic constituents. Recently, we have started research to simultaneously analyze the metallic and organic constituents in fossils, soil, PM2.5, tissue, alloy, etc. by sequential ionization MS.

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Conflict of Interest

The authors declare no conflict of interest.

Author details

Jiaquan Xu[1] and Huanwen Chen[1,2]*

1 Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China University of Technology, Nanchang, P. R. China

2 School of Pharmacy, Jiangxi University of Chinese Medicine, Nanchang, P. R. China

*Address all correspondence to: chw8868@gmail.com

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