**Application of ICP-MS in the Innovation and Practice of Instrument Analysis Course - Taking the Determination of Cesium in Soil as an Example**

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**Abstract.** Instrumental analysis is an important part of analytical chemistry, which plays a crucial role in cultivating the experimental operation ability of students in disciplines such as environment, geology, and medicine. Inductively coupled plasma mass spectrometry (ICP-MS) is currently an irreplaceable basic equipment in inorganic element analysis, and incorporating it into experimental teaching content is a requirement of the times. However, there is still a lack of application in this area. This article focuses on the graduate course "Modern Detection Technology". The experimental course adopts a mixed teaching mode of pre class theoretical guidance and in class emphasis on practical operation. It combines theoretical and practical teaching organically, and takes the current hot topic of radioactive pollution as the problem orientation. The teaching mainly focuses on analyzing experimental design, instrument operation and use, sample measurement and result analysis, etc. The teaching mode and content of ICP-MS continuously explored to improve the quality of experimental teaching and enable students to comprehensively enhance their basic skill knowledge, scientific research literacy, and innovation awareness.

1. Introduction

Analytical chemistry is an important foundational course in the field of analytical methods and theories for studying chemical information such as composition, content, structure, and morphology of substances. Instrumental analysis is an important aspect of analytical chemistry. This course has presented the characteristics of an era of interdisciplinary integration and development with multiple disciplines such as environmental science, geology, materials science, pharmacology, and biology [1,2]. With the rapid development of China's national economy, the quality of undergraduate basic education has been rapidly improved, and theoretical curriculum education has also been continuously reformed and innovated [3]. Among them, experimental teaching is an important component of theoretical course teaching, which is an important way for students to absorb, digest, consolidate and expand classroom theoretical knowledge. It is also an important link in cultivating students' scientific research thinking ability and problem-solving ability [4,5]. Experimental teaching plays a crucial role in the talent cultivation of chemistry related majors [6], and the reform of experimental course teaching is also urgent.

However, the reform of experimental teaching in analytical chemistry lags behind the reform of theoretical teaching, with fewer experimental classes and often only simple confirmatory experiments and instrument operation exercises, such as titration and buffer analysis experiments, which cannot be in line with the era background of rapid updating of modern analytical instruments. All along, the teaching methods for analytical chemistry experiments have been relatively fixed. For example, specialized teaching assistants place experimental instruments and consumables in advance on the experimental platform based on the experimental content. The experimental teaching teacher uses multimedia and blackboard writing for rote teaching. After the experimental teaching is completed, each group of students write an experimental report based on the teacher's explanation and demonstration, and obtain the expected results, and teachers grade based on experimental results and reports. Although this traditional teaching model can ensure smooth experimental progress, it often constrains students' enthusiasm and creativity, making it difficult for them to master existing analytical methods and instruments. Once encountering new problems, they may find it difficult to start. This is far from the requirements of cultivating innovative talents advocated by the country. In addition, many universities use outdated analytical and measurement instruments in experimental teaching. For instruments such as inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatography-mass spectrometry (GC-MS) that are commonly used in scientific research, most of them only introduce detection principles and explain operating procedures, and rarely allow students to operate the instruments manually [7,8].

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The monotonous and unchanging teaching methods and models can no longer meet the needs of cultivating analytical chemistry talents in the new era, and universities urgently need to explore new teaching methods. One of the difficulties in the current reform of analytical chemistry experimental teaching is how to efficiently achieve teaching objectives and improve students' learning interest and research thinking ability under limited class hours, equipment, and funding conditions [9]. ICP-MS is a commonly used instrument for trace and ultra trace element analysis, which has been widely used in sample analysis in fields such as environment, geochemical composition, medicine, and public health [10]. It is necessary to introduce the teaching content of ICP-MS operation in analytical chemistry experiments during the undergraduate stage. This article explores the introduction of ICP-MS into the teaching of analytical chemistry experiments, and reforms the teaching of analytical chemistry experiments through measures such as updating teaching modes, optimizing course content, and improving assessment methods.

With the development of industrial level, metal pollution in soil is becoming increasingly serious [11,12]. Therefore, this course is guided by the specific issue of detecting cesium in soil environment, introducing large-scale instrument ICP-MS to upgrade traditional experimental teaching, achieving "less but more precise, more precise and new" in teaching content, align with the forefront of science, expand students' thinking, broaden their horizons, and stimulate their interest in learning, to achieve good experimental teaching results.

2. Experimental section

Taking the graduate course "Modern Detection Technology" as the research object, the students will be divided into groups of three in advance. The teaching teacher will send basic knowledge such as instrument principles, structures, applications, and sample processing to students in advance through WeChat through pictures and videos. Students can ask questions about the basic knowledge of ICP-MS at any time, and the teaching teacher will provide answers 2 days before class after collecting students' difficult points. This pre class preview can effectively supplement the experimental teaching content that cannot be offered offline due to factors such as class hours and venue, and improve teaching efficiency. The teaching teacher presents the problems that need to be solved in this class before the experimental class, allowing students to conduct experiments with the problems, fully mobilizing their exploration enthusiasm and increasing the fun of the experiment. After class, each group selects a team leader to give a speech and summarize the experimental situation of the group. Teachers can try to establish a comprehensive evaluation and assessment model to replace traditional experimental reports or test papers. In addition to writing experimental reports, students are also required to create a group based experimental summary PPT to showcase the experimental plan, results, data analysis, and instrument usage experience.

3. Specific example - detection of ultra trace cesium in soil by ICP-MS

3.1. Principle of ICP-MS

Before conducting the experiment, briefly introduce the principle and structure of ICP-MS and provide answers to the questions of the students. The working principle of ICP-MS is that the sample of the test solution is transformed into an aerosol state through the atomization system, and enters the central region of the ICP plasma under the action of the carrier gas (Ar). It undergoes steps such as dissolution, gasification, and ionization to become positively charged ions; The ions enter the detector through off-axis, focusing system, and quadrupole screening system, and display the count values per second related to the sample concentration on the computer to achieve accurate quantitative analysis of elements in unknown samples.

3.2. Instruments and materials

The instruments and reagents used in this experimental course are as follows: ICP-MS (PlasmaQuant MS, Analytik Jena, Germany); High purity helium and argon (≥ 99.999%); $^{133}$Cs stock solution and $^{103}$Rh internal standard solution (1000 μg/mL) were purchased from Shandong Metallurgical Science Research Institute Co., Ltd; Hydrochloric acid, nitric acid, hydrofluoric acid, and perchloric acid were purchased from Beijing Chemical Plant; Ultra-pure water (resistivity 18.2 MΩ); The containers were soaked overnight in 20% nitric acid (V/V) and then rinsed clean with ultrapure water for later use.

3.3. Preparation and processing of samples

In this teaching, a certain amount of cesium stable isotope ($^{133}$Cs) solution is added to clean soil to prepare samples. After drying the prepared soil, weigh 0.2000 g of sieved soil sample and place it in a 50 mL polytetrafluoroethylene crucible. After wetting with a small amount of water, add 10 mL of hydrochloric acid, 5 mL of nitric acid, 10 mL of hydrofluoric acid, and 2 mL of perchloric acid in sequence. Then, the mixed solution is heated at 160°C on an electric heating plate for 6 h, and up to 280 °C to exhaust the white smoke of perchloric acid. 15 mL of newly prepared (1+2) aqua regia is added and the salt is dissolved at high temperature. After cooling, the above mixed solution is transferred to a 50 mL volumetric flask for measurement. Blank samples is prepared simultaneously with the sample.
3.4. Optimization of working conditions

After the mass spectrometer is ignited and stabilized, the instrument parameters were debugged and optimized using a tuning solution of Be, Co, In, and U at a concentration of 10 μg/L. The sensitivity, oxide, and double charge yield of the tuning elements were used as evaluation indicators to optimize the instrument parameters, adjust the instrument sensitivity, resolution, and stability, and determine the optimal working conditions of the instrument. Under these conditions, cesium had the highest single charge ion strength, while oxides and double charge yields are the lowest. After the tuning of instrument was completed, the instrument parameter settings were determined.

3.5. Precautions during sample testing process

Before testing the sample, it is necessary to select internal standard elements, which are crucial in mass spectrometry detection. The principle of selecting internal standard elements is that the solution being tested does not contain the internal standard element, the interference factors of the internal standard element are minimized, and the mass spectrometry behavior is as consistent as possible with the measured element, which can effectively overcome matrix effects. Due to the above reasons, the internal standard element selected in this course teaching is 103Rh. Interference is inevitable in ICP-MS determination, mainly including matrix interference and mass spectrometry interference. During the teaching process, attention should be paid to guiding students to adopt appropriate methods to reduce interference. In this course, the use of three-way valves to add samples and internal standards online can effectively correct instrument interface effects and matrix effects. The mass spectrometry interference of cesium elements is mainly caused by the interference of oxides and double charge isomers. By optimizing instrument parameters, its mass spectrometry interference can be minimized to the greatest extent possible.

3.6. Analysis of detection results

3.6.1. Limit of detection

In this experimental teaching, a standard method is used to calculate the limit of detection (LOD). The specific operation is as follows: 11 blank solutions are continuously measured, and the standard deviation of their concentration is calculated. The detection limit is recorded as 3 times the standard deviation, and the quantification limit is recorded as 10 times the standard deviation. The experiment found that LOD of this method was 0.003 μg/g.

3.6.2. Accuracy and precision of the method

In the experiment, the accuracy and precision of the detection method were calculated by 6 repeated measurements of the soil sample digestion solution. The results showed that the average value of 133Cs was within the reference range, indicating good accuracy. The relative standard deviation (RSD) of the 6 repeated measurements was all within 5%, indicating good precision of the method.

3.6.3. Recovery rate of spiking

0.5 mL of each pilot sample was taken to mix evenly. The mixed sample was divided into 7 parts. One part of the mixed sample was processed and tested directly, while the other 6 parts were added with a mixed standard solution containing the elements to be tested. After processing under the same conditions, the 7 samples were tested. The results showed that the recovery rate of 133Cs was between 91.9% and 108.2%.

3.6.4. Quantitative analysis of 133Cs in unknown samples

Before class, 6 soil samples were prepared, and different concentrations of 133Cs solution were added to each sample. Then the soil sample was dried. The students used the ICP-MS method established above to continuously measure cesium elements in 6 soil samples with unknown 133Cs content three times, and the teacher evaluated the measurement results. Moreover, the students were required to summarize the problems encountered during the experiment, propose solutions, and finally write an experimental report.

4. Reflection after class

4.1. Design of experimental courses

Due to the tedious and difficult to understand basic knowledge of ICP-MS, as well as the complex operation and maintenance procedures, it is difficult for students to master the flexible use of ICP-MS in a short period of time through a single theoretical explanation or traditional observation and experimental teaching. Moreover, a large amount of boring content will seriously affect students' enthusiasm and is not conducive to the cultivation of innovation ability. Therefore, this experimental course is based on the precision instrument four pole ICP-MS and the chemistry professional background of students. The experimental project is designed to integrate the basic knowledge and experimental skills of ICP-MS. Through pre class preview of students and pre class Q&A by the teaching teacher, students are familiar with the main structure, working principle, daily maintenance, and design points of such experiments of ICP-MS, solidifying their theoretical foundation and ensuring the smooth progress of practical teaching; Practical operations deepen students' understanding of ICP-MS theoretical knowledge, consolidate the validation procedures and sample analysis process of general
methodology, and fully mobilize their subjective initiative to improve teaching quality.

In addition, the pre-treatment of soil samples - acid digestion method, is relatively simple. However, in practical research projects, students may encounter samples that are difficult to process using only acid digestion methods, such as geochemical samples, metal minerals, etc. This requires students to consult references and organize experimental plans based on the operational skills of this experimental course. So, in the teaching process, a gradual approach can be adopted to fully utilize students' self-learning ability, stimulate their scientific research thinking, and improve the quality of experimental teaching. Due to the high purchase price and operating cost of ICP-MS instruments, as well as the high-precision characteristics of the instruments, teachers need to arrange students' operation and use of ICP-MS reasonably, and control the operating time of the instruments. Moreover, emphasis should be placed on the maintenance and upkeep of instruments to reduce human caused instrument malfunctions. Compared to the traditional experimental teaching mode of teacher demonstration and student observation, the large-scale instrument experimental teaching mode based on experimental projects is more easily recognized and accepted by students. This is undoubtedly a beneficial attempt to explore the teaching methods of large-scale precision instrument experiments.

4.2. Design of course content

Given the time constraints of experimental courses, the selection of course content is crucial, ensuring both the quality of experimental teaching and the completeness of teaching content. Firstly, basic theoretical knowledge is essential, including the main structure and working principle of ICP-MS, optimization of instrument working conditions, and daily maintenance of the instruments. This section covers the basic requirements for operating ICP-MS instruments, mastering the use of such cutting-edge large-scale instruments proficiently, laying a solid foundation for students' future scientific research, and improving their social competitiveness to a certain extent. Secondly, the elimination of various interferences during ICP-MS elemental analysis. The reduction and elimination of various interferences are directly related to the accuracy of measurement results [13,14], which is also the difficult content of this experiment. By introducing such knowledge points through specific experiments, students can gain a deeper understanding of ICP-MS technology in a way that is easy for them to accept. Moreover, it can activate their thinking and deepen their understanding of the working principles of instruments and the key and difficult points in experimental design. This often cultivates students' scientific research literacy more than the experiment itself, expanding the value of ICP-MS experimental teaching. Once again, the validation procedures and sample analysis processes of general methodology include linear relationships, detection limits, quantification limits, precision, accuracy, recovery rates, etc. This section reflects the framework of the entire experiment and consolidates the design ideas of analytical experiments. The experimental projects and other sample analyses involved in ICP-MS serve as knowledge expansion content or open experiments, broadening students' research perspectives and inspiring their innovative thinking.

4.3. Experimental assessment and feedback

In the experimental teaching of ICP-MS, obtaining accurate test results of experimental samples is not the primary goal of teaching. The truly important teaching goal is to enable students to master the operation and application methods of the instrument, and obtain the ability to analyze and solve problems from it. Therefore, after the experimental class, in addition to allowing students to write simple experimental reports, an assessment method in the form of defense can also be added, allowing each group to select one student to give a report. The report content includes instrument principles, result discussions, phenomenon analysis, instrument operation precautions, etc. The teaching teacher randomly questions the students in the group on site based on the data and report situation, and scores them based on the report and Q&A situation. Each student in the top ranked group will receive an additional formative assessment score. Under this assessment form, all students in the experimental classroom will participate in the design of the experimental plan, instrument operation, result analysis, and discussion, and their enthusiasm will be fully mobilized. Student feedback after class indicates that this teaching and assessment method has enabled them to truly master the operation and flexible use of instruments, exercise their research thinking, and lay a foundation for their future scientific research. In addition, reporting and defending between different groups is also a form of exercise for students' logical thinking and eloquence.

5. Conclusion

Using experimental projects as a carrier, ICP-MS is applied to the teaching of analytical chemistry experiments in universities, effectively cultivating students' practical operation ability and comprehensive scientific research literacy. This article focuses on the graduate course "Modern Detection Technology" and optimizes the teaching content and methods. Firstly, the basic structure, detection principles, daily maintenance, and other theoretical knowledge of ICP-MS is taught through pre class preview and Q&A. Secondly, taking the detection of cesium in soil samples as an example, students form a group of three people to design and implement experimental plans for sample processing, analysis and detection, data processing, and other experimental content. Then, each group will report the experimental results and defend against the questions raised by the teaching teacher. Finally, reflect on the course design, teaching content, student feedback, and assessment format are conducted after class. In this
article, ICP-MS is applied to teaching through theoretical explanation and practical operation, effectively improving teaching quality from basic knowledge, experimental design, and large-scale instrument operation skills. However, some problems have also been found in the implementation of teaching, such as students being prone to pollution during the experimental process due to lack of experience, and students lacking practical operation to maintain the sampling system due to classroom time constraints. These to some extent hinder the cultivation of students' ability to operate ICP-MS independently throughout the entire cycle. Although there are still some shortcomings in this experimental course, through practice and exploration, the teaching of this experiment will continue to be improved and enhanced to better serve the talent cultivation of universities.

References


