Development of the Split Type Ion Chromatograph

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Abstract: In the analysis of nuclear fuel process, the analysis of the anion content in the solution has always been a difficult problem. Ion chromatographs cannot be used directly for the measurement of anions in radioactive samples, so the split type ion chromatograph is necessary. The instrument is divided into two parts: the host and extension. The host is the part that is not in contact with the radioactive samples and is placed outside of glove box. The extension is the part that is in contact with the radioactive samples and is enclosed in glove box. The host and extension of instrument are connected by the lengthened wire, signal wire and eluent pipeline. The extension is mainly made of stainless steel, with the components of ion chromatograph regularly arranged on the stainless steel bracket. The split type ion chromatograph is installed in the glove box and the main performance indicators are tested. The baseline noise is less than 0.3%FS and baseline drift is less than 2.0%FS. The qualitative repeatability of the instrument is better than 0.02%, and the quantitative repeatability of the instrument is better than 0.7%. The split type ion chromatograph has a good application prospect in nuclear fuel process analysis.

1. Introduction
With the development of nuclear industry, the importance of nuclear fuel cycle becomes increasingly obvious. Nuclear fuel post-treatment is an important link in the closed nuclear fuel cycle system, and post-treatment process analysis is an important part of post-treatment technology. Nuclear fuel reprocessing is a chemical process to extract uranium and plutonium from spent fuel according to the differences of distribution ratios of uranium, plutonium, fission products and other impurities in the TBP-n-dodecane (or kerosene) phase and water phase. On the current international mainstream the spent fuel reprocessing process uses PUREX (Plutonium and Uranium Recovery by Extraction) process [1]. In this process, the samples analyzed at each monitoring point are highly radioactive, so the sample measurements are generally carried out in the glove box. Among them, the post-treatment process of anions including nitrate ion and oxalate still adopts volumetric method and spectrophotometry [2] and other traditional analysis method. However these methods generally have low sensitivity, high capacity of samples and are too complicated to operate, and other shortcomings, and even the phenomenon of low content of the object under test to measure, lack of rapid and sensitive analysis method for a long time. Therefore, trace anion analysis in post-treatment process is always a difficult problem to be solved.

Ion chromatography is a kind of high performance liquid chromatography (HPLC). As a routine anion detection technology, it is widely used in the qualitative and quantitative analysis of various organic anions and inorganic anions in solution. It has the advantages of good selectivity, high sensitivity, low detection limit and simultaneous determination of multiple components. However, due to the highly radioactive characteristics of post-treatment samples, commercial ion chromatograph cannot be used directly, which limits the application scope of ion chromatography in post-treatment analysis, and ion chromatography has not really functioned. In view of the difficulty of application of...
ion chromatography to the measurement and analysis of highly radioactive samples, Chen Lianzhong et al., from China Institute of Atomic Energy Research, developed a domestic closed-type ion chromatograph [3], which can be used for the measurement of anions and cations in radioactive samples. However, as the instrument is divided into inner box and outer box and the material of the box is plastic, it has poor acid-resistance and irradiation-resistance performance. And the instrument is of large volume, so a customized glove box is needed. At the same time, with the development of ion chromatograph, its data processing system has fallen behind. In this thesis, through studying the analysis principle of ion chromatograph and the structure and working principle of each component [4], combined with the existing conditions of the unit and the final application requirements, the EP-1000 ion chromatograph produced by Liyuan Electronic Instrument Co., LTD is modified. The arrangement of each component of the instrument is redesigned and processed, and the split-type ion chromatograph which can be closed in the glove box is developed to solve the problem of trace anion chromatographic analysis in highly radioactive samples and expand the application of ion chromatograph.

2. Design of split ion chromatography

2.1 Design requirements of instruments
With Liyuan EP-1000 ion chromatograph modified to become a split type ion chromatograph, the equipment is installed in the post-processing analysis in the laboratory. Due to the laboratory glove box has been installed already and have been put into use, glove box is full of acid gases and plutonium aerosols, which has strong corrosiveness to the instrument, causing the instrument destroyed and become radioactive waste. Therefore, the design of the split-type ion chromatograph must meet the operation requirements of the glove box in the post-processing analysis laboratory. First, for the installation of the extension part of the instrument, the extension can only be transferred into the glove box through the glove hole on the glove box without removing the back plate of the glove box. The connection wire, signal wire and eluent pipeline between the main machine and the extension machine can only be connected from the outside through the reserved holes on the glove box, so as to avoid the leakage of radioactive substances during installation. Second, reduce the use of electronic components in glove boxes. Since acidic gases and plutonium-containing aerosols can corrode electronic components such as solenoid valves, it will become radioactive waste once damaged. Third, the design is simple and easy to operate. Each component of the ion chromatography placed in the glove box should be easy to install, replace and link. Fourth, the extension inside the glove box is controlled by the host outside the glove box.

2.2 Overall structural design
Ion chromatographic instrument generally consists of eluent conveying system, sampling system, separation system, inhibition system, detection system and data processing system. Its working process: leachate pump delivers the eluent evenly to the separation system, through the sample system in front of the chromatographic column (usually by six-valve valve replacement flow switch) eluent to send samples to the chromatographic column; each component in the chromatographic column is firstly separated, and as the eluent passing suppressor in turn is sent to the detector to detect, and its software system is used for data analysis and processing. In the working process, several parts of the sampling system, separation system, inhibition system and detection system of the instrument will be contaminated by direct contact with radioactive samples. These parts of the instrument will be sealed in the glove box, so as to realize the analysis of radioactive samples by ion chromatography.

The ion chromatograph is divided into two parts. One part is enclosed in the glove box, and the other part is placed outside the glove box, which is designed as a split-type ion chromatograph. The main body of the split ion chromatograph includes circuit board, circuit control element, eluent conveying pump, eluent tank, data processing and other components, which are placed outside the glove box. The extension of the instrument includes injection valve, quantitative ring,
chromatographic column, suppressor, conductance detector, waste liquid pipe, waste liquid tank and support, which are enclosed in the glove box. Figure 1 shows the structure of the split ion chromatograph. The main body of the split ion chromatograph includes circuit board, circuit control element, eluent conveying pump, eluent tank, data processing and so on, which still uses the original accessories of Liyuan EP-1000 ion chromatograph. The sample injection valve, suppressor and conductance detector of the extension are modified to meet the needs of applications in the glove box.

Fig. 1 Structure diagram of the split type ion chromatograph

2.3 Structural design of extension

The design of the split type ion chromatograph is to meet the requirements for installation and application of the above-mentioned glove box, and the structural design of the split type ion chromatograph is shown in Figure 2. The specific materials and design are as follows:

1) The main material of extension is stainless steel 316L with corrosion resistant and irradiation resistant. Its base and support are all made of stainless steel material, with injection port, six-way valve surface, inhibitor and conductivity detector wrapped in stainless steel material, and the sharp angle of stainless steel support is passivated to prevent scraping thick wall gloves on glove box and causing radioactive material to leak out.

2) The extension base is designed to be round, with small overall volume. The upper stainless steel support can rotate, and can be transferred into the glove box through the glove hole;

3) The six-way valve is manual injection mode, wrapped with stainless steel, with acid-resistant and alkali-resistant polyether ether ketone (PEEK) material used internally, and the rotating handle is enlarged, which is easy to operate in the glove box.

4) The wire and signal line inside the glove box are wrapped with acid and alkali resistant protective material, and the quick connection plug is used to connect with the extension, and the connection joint is closed with vacuum glue.

5) The inhibitor and detector on the extension use the membrane inhibitor and conductivity detector produced by Liyuan Company. The conductor cell is made of PEEK material, and the electrode is 316 stainless steel. In order to facilitate the installation and reduce the instrument volume, the inhibitor and the detector are connected together, with the shell wrapped in stainless steel. The wire outlet is sealed with silicone rubber, and the wire plug is a quick connection plug.

6) The injection port, six-way valve, chromatographic analysis column, inhibitor and conductivity detector are installed on the front panel of the bracket, and are connected in turn by pipes made of PEEK material.
3. Performance of split Ion Chromatography

The split ion chromatograph is installed in the post-processing radioactivity laboratory; the extension is installed in the glove box; the main engine and the computer are placed outside the glove box; the washing fluid pipeline, the wire and the signal line reach into the glove box through the original small hole in the glove box, and then are closed with flange to connect the flow circuit joint and circuit joint reserved on the instrument extension respectively, and the waste liquid of washing liquid flows into the waste liquid tank in the glove box. In order to ensure the measurement reliability of split ion chromatograph, the performance of split ion chromatograph after installation and closure is tested before use.

The measuring conditions of ion chromatography are as follows: the quantitative ring is 100 μL, the eluent is 30mmol/L sodium hydroxide solution, the flow rate of eluent is 0.6 mL ·min, the chromatographic column is IonPacAS11-HC anion exchange column (250mm × 4mm) and AG11-HC protective column (50mm × 4mm), Thermo Company, USA; suppression conductivity detector (Beijing Liyuan Company), suppression current 76 Ma. Experimental data collection and system operation using Liyuan EP-1000 chromatographic workstation.

3.1 System leak-free inspection

The pump, injection valve, chromatographic analysis column, inhibitor and conductivity detector of the split ion chromatograph are connected well. Sodium hydroxide aqueous solution is used as the mobile phase to start the instrument. Within the allowable pressure range, the water absorption paper is used to check the joints of the pipeline for no wet trace, which proves that there is no leakage in the system.

3.2 Base line noise and base line drift verification

The sensitivity of the split ion chromatograph is adjusted to 10 μs, the peak height of chloride ion of 0.50mg/L as the full scale, and the instrument runs for 40 min. The baseline noise and baseline drift are detected as shown in Fig. 3. After measuring and calculating, the baseline noise is 0.3% FS; The baseline drift is 2.0% FS.
3.3 Minimum detection concentration

Improve the sensitivity of the instrument to have obvious noise, select the chloride ion concentration of 0.50mg/L, and determine the peak height of the injection sample. The minimum detection concentration of the ion to be measured can be calculated according to formula (1):

$$C_{\text{min}} = C_s (2HN/H)$$  \hspace{1cm} (1)

$C_{\text{min}}$ in the formula is the minimum detected concentration (mg/L); $C_s$ is the detection ion concentration (mg/L); $H$ is the peak height of the detection ion (mV); and the $HN$ is the base line noise (mV, not less than 30 min baseline). Under the condition of NaOH as the eluent, the ion chromatography-based line noise is determined, and then the chloride ion of 0.50 mg/L is measured, and the peak height of the base line noise of the ion chromatogram and the chloride ion of 0.50 mg/L are respectively substituted into the formula (1) to calculate the detection limit of the chloride ion to be 0.005 mg/L.

3.4 Qualitative repeatability and quantitative repeatability

The chromatographic peak retention time, peak height and peak area of each injection are obtained by selecting chloride ion of concentration 0.50mg/L for 6 consecutive times. The results are listed in Table 1. The relative standard deviation is calculated as the basis of qualitative reproducibility of chromatography, and the relative standard deviation of chromatographic peak area (or peak height) is calculated as the basis of qualitative reproducibility of chromatography. The qualitative reproducibility and quantitative reproducibility of split ion chromatography are 0.02% and 0.7%, respectively.

| (samples) | (Retention time) / (min) | (Peak height)/ (mV) | (Peak area) (mV*s) |
|-----------|--------------------------|---------------------|-------------------|
| 1 #       | 8.170                    | 289.861             | 6532.854          |
| 2 #       | 8.171                    | 290.089             | 6515.076          |
| 3 #       | 8.169                    | 289.041             | 6603.433          |
| 4 #       | 8.172                    | 290.600             | 6606.174          |
| 5 #       | 8.173                    | 290.743             | 6600.859          |
| 6 #       | 8.172                    | 291.731             | 6623.472          |
| RSD/%     | 0.02                     | 0.4                 | 0.7               |

According to the verification requirements of ion chromatography, the basic line noise of the instrument conductivity detector is 2% FS, the base line drift is 20% FS/30 min, the minimum detection concentration is 0.02. mu. g/ mL, the qualitative repeatability of the instrument complete machine performance is not more than 1.5%, and the quantitative repeatability is not more than 3%. As we can see from the above data, the performance of the split type ion chromatograph and the detection result of the conductivity detector meet verification requirements of the ion chromatography.

4. Conclusion

The split-type ion chromatograph developed in this study is divided into two parts: host and extension.
The instrument unit is enclosed in the glove box, and the main unit can be controlled outside the glove box. The unit enclosed in the glove box is convenient for installation, to be disassembled and assembled, and operation. The material is corrosion-resistant and irradiation-resistant, and meets the long-term use requirements in the glove box. The baseline noise of the enclosed split ion chromatograph is 0.3%FS; Baseline drift is 2.0%FS; Minimum detected concentration: ≤0.005μg/mL; Qualitative repeatability is 0.02%; Quantitative repeatability is 0.7%; The overall performance of the instrument is stable and can meet the application requirement of sub-chromatography. The instrument has been installed in the laboratory of post-treatment radioactivity analysis, and has been used for the measurement of trace oxalate, nitrate and other anions in post-treatment samples, and the measurement results are reliable. Therefore, the closed and separated ion chromatograph can be satisfied for the chromatographic analysis of anions in nuclear fuel reprocessing process solution and high level radioactive waste liquid, and has a good application prospect in nuclear fuel process analysis.

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