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RESEARCH PAPER

Development and Evaluation of On-line Eluent Generator

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Abstract: Electrodialytic eluent generator, one of the key components of ion chromatography system, was fabricated and evaluated. The data achieved indicated that its performance could be comparable to that of commercial one. The maximal operation pressure was over 20 MPa, the generated KOH concentration was up to 100 mM, and the designed usage lifetime was about 354 day (take 8 h working time per day). This device will be helpful to the improvement of domestic instruments of ion chromatography.

Key Words: Ion chromatography; On-line eluent generator; Potassium hydroxide; Anions

1 Introduction

Ion chromatograph (IC) has been a well-established technique for the analysis of ionic species since it was introduced in 1975[1,2]. A distinct feature of IC relative to common liquid chromatography is strong base or strong acid used for eluent. Manual preparation of such kind of eluents often leads to operation error, especially for strong base eluents (e.g. KOH). The reason is that these eluents are easily contaminated by carbon dioxide and the final generated carbonate has much stronger elution strength relative to hydroxide, leading to poor reproducibility and detection. Such problem was thoroughly solved by the use of electrodialytic eluent generator (EDG)[3–5]. The working principle of EDG is based on electrodialysis and the pure water can be online transformed into high purity eluent via electrodialysis, which avoids the possible operation errors of manual preparation and possible contamination and makes the whole system easy automation, resulting in enhanced operation reproducibility and sensitivity of the whole equipment[3,6,7].

EDG was commercialized in 1998 by Dionex Corp[3] and now has been a key component of state-of-art IC system of Dionex. Although the research of IC technique and the related instrument of China started in 1980s, the EDG has still not been reported. Here three kinds of high pressure EDG were successfully fabricated and evaluated in detail. The data indicated that their performance could be comparable to that of commercial ones.

2 Experimental

2.1 Regents

The standard samples including NaF, KCl, KBr, $NaNO_3$, and Na_2SO_4 were purchased from Aladdin regent Corp. (Shanghai, China). KOH feed solution was from Sigma Corp. (USA). Ultrapure water was obtained through a Millipore water purification system (USA).

2.2 Principle and device of EDG

Take KOH EDG as example, its configuration is schematically shown in Fig.1 and its working principle is as follows. EDG device consists of EDG cartridge and associated components including non-hydroxide anion removal device, degasser and a program-controllable constant current source. EDG cartridge is the heart of EDG and it is composed of KOH regenerant chamber, cation exchange membrane and eluent channel. The regenerant chamber and eluent channel are isolated by cation exchange membrane, which functions to prevent bulk liquid from eluent channel into regenerant chamber and allows cation migration as well. Anode and cathode are placed in the regenerant chamber and the eluent channel, respectively. When pure water driven by high pressure pump is flowing through the eluent channel, potassium ions are migrated into the eluent channel across cation exchange

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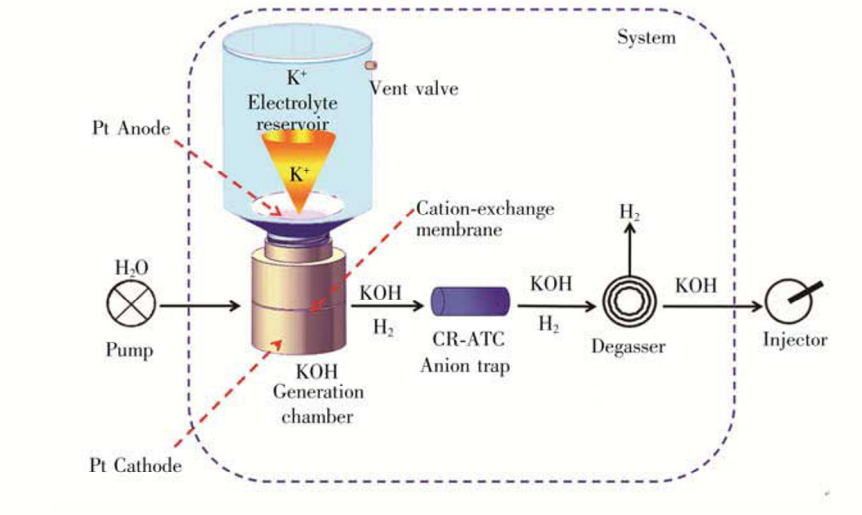

Fig.1 Schematic diagram of KOH generator

membrane, to combine the hydroxide produced in the eluent channel due to water splitting into KOH under a given current. The produced KOH concentration is highly correlated with the applied current. Thus the KOH concentration required can be easily controlled by the adjustment of applied current. As shown in Fig.1, non-hydroxide anion removal device is used to remove any possible non-hydroxide anions (mainly from the pure water). The degasser function is to remove the electrolytic gases (hydrogen in this case). If KOH in the regenerant chamber is changed into methanesulfonic acid (MSA), cation exchange membrane is replaced by anion exchange membrane, and the electrode polarity is switched, the above KOH EDG can be changed into a MSA EDG, for the cation analysis.

3 Results and discussion

3.1 Pressure tolerance

Because EDG is placed between high pressure and injector in the typical IC configuration, it has to be capable of bearing high pressure enough to meet the requirement of IC system. Here the pressure tolerance of the fabricated EDG was tested as follows. It was connected with a packed column and the produced backpressure at different flow rate was plotted with flow rate. Good linearity was observed for the tested flow rate range ($R^2 > 0.991$), indicating good mechanical stability of the EDG. The results show that the EDG can tolerate at least 21 MPa of pressure, which was equal to that of commercial one. Such range could meet the majority of analysis requirements.

3.2 Performance evaluation

The performance of KOH EDG was evaluated in terms of current efficiency, concentration gradient, purity and running stability. Because EDG was based on the electrolysis of pure water, the produced KOH concentration was proportional to the applied current. As shown in Fig.2, the produced KOH concentration had good linearity with the applied current. The slope of the fitted curve between KOH concentration and applied current at the flow rate of 1 mL min^{-1} was about 0.623, which was much close to the value 0.621 calculated by Faraday's law. The results indicated that the fabricated KOH EDG had almost ideal current efficiency.

The KOH concentration generated at different current is illustrated in Fig.3. The maximal tested KOH concentration

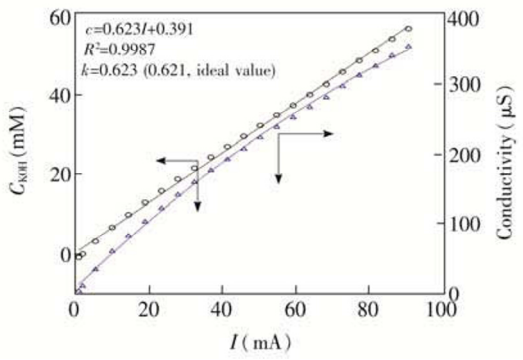

Fig.2 Relationship of the applied current and the generated KOH concentration and conductance

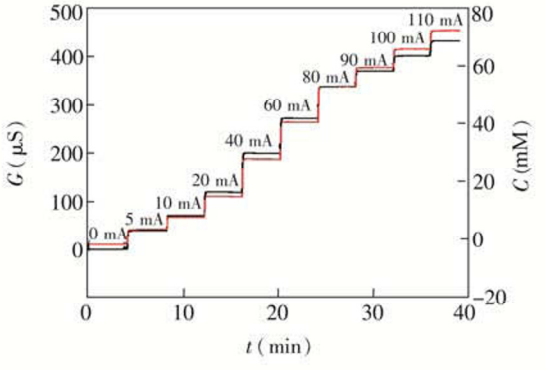

Fig.3 Concentration gradient of KOH generator