Rapid Separation and Determination of Organic Acids in Bauxite by RP-HPLC after Solid-Phase Extraction

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A rapid revised phase-high performance liquid chromatographic (RP-HPLC) method for the determination of organic acids in bauxite was reported. Oxalic, malonic, acetic, succinic, glutaric and adipic acid were separated and quantified in 10 min. First time repeatability, reproducibility and recoveries were determined out for these acids in bauxite. The organic acids were removed from bauxite by using a solid-phase extraction procedure with anion-exchange cartridges. The chromatographic separation was achieved with only one Kromasil RP-C$_{18}$ column thermo stated at 25 °C. Organic acids were detected with a UV–vis detector (215 nm). The precision results showed that the relative standard deviations of the repeatability and reproducibility were <2.13% and <3.24%, respectively. The method accuracy was confirmed with an average recovery ranging between 89.2 and 114.7%. Under optimum conditions, the detection limits ranged from 0.042 to 10.36 mg/L.

Keywords: organic acid, determination, bauxite, RP-HPLC

The bauxite from which the alumina is refined generally contains organic carbon, ranging from intact plant material to decayed plant and animal remnants. The Bayer process can be summarized as the digestion of bauxite with caustic liquor and the subsequent precipitation of hydrated alumina[1]. Most bauxite contains organic matter in various amounts. The major source of organic matter that is introduced into the Bayer liquor is from the bauxite in the form of organic substances. During the digestion, the organic matter is dissolved, degraded and oxidized with the results that the liquors darken, and notable amounts of oxalate and carbonate are formed. Due to the acidic nature of the organic substances, an important quantity of the organic matter contained in the bauxite is extracted into the liquor. The principal degradation products are sodium oxalate and sodium carbonate. Depending upon the digestion conditions, typically 5-10% of the organic carbon is converted into sodium oxalate. Australian bauxites have conversion rates of two or three time's higher [2-3]. In the Bayer process the caustic liquor is recycled, and because of this the organic matter builds up to an equilibrium level, typically to 10-30 g/L of organic carbon content, determined by the outputs and the inputs [4]. The organic substances have been shown to be very harmful with regard to alumina productivity and size [5-6]. These organic carbon compounds can have a detrimental effect on the alumina refinery process by: (1) reducing the productivity of the caustic soda solution (or liquor) used to dissolve alumina-bearing minerals, (2) affecting product quality, (3) disrupting plant operation, and (4) causing volatile organic carbon emissions. If the organic substances could be removed from the Bauxite sample before Bayer process, it is very helpful for industry. The evidence suggests that organics contamination could be costing these refineries several hundred million dollars a year. So the rapid and reliable determination of organic acids in Bauxite is of significant industrial importance. The analysis of organic acids in Bauxite with HPLC systems is a difficult task due to high ionic strength and pH. Our particular interest concerns the development of a simple HPLC procedure for the determination of organic acids levels in bauxite. A method method was successfully applied to analysis of bauxite samples from Laos.

Experimental part
Chemicals and standards

Analytical standard-grade oxalic, malonic, acetic, succinic, glutaric and adipic acid were obtained from Sigma (St. Louis, MO, USA). Stock standard solutions were prepared by dissolution of acids in Milli-Q water; they were stored at 4 °C for 1 month. The Milli-Q water was purified by passage through a Compact Milli-RO and Milli-Q water system from Millipore (Milford, MA, USA). Working standard solutions were prepared daily by dilution with Milli-Q water. Potassium dihydrogenphosphate, sodium hydrogen carbonate, orthophosphoric and hydrochloric acid were Analar grade and supplied by Shanghai (Shanghai, China).

The samples were filtered through cellulose membrane filters Whatman (0.45 μm, Whatman, Clifton, NJ, USA). The eluent was filtered with membrane filters Phenomenex (0.45 μm, AFO-0504, CA, USA).

Apparatus

Chromatographic analyses were carried out using a Waters liquid chromatograph (USA) equipped with a Waters ILD on-line degasser, a Waters 600E pump, a Waters 717 plus auto sampler and a Waters 996 diode-array UV detection system (Waters). The detector signals were recorded on a chromatography data system MILLENNIUM 32®. The column was a Kromasil RP-C$_{18}$ (250 × 4.6 mm I.D., particle size 5 μm, Hanbon Science &Technology Co., Ltd). A PHS-3C pH meter (Shanghai, China) was also used.

Sample preparation

Organic substances were extracted from 1 kg of air-dried bauxite collected from Champasak (Laos) by caustic digestion. Calcium carbonate was removed from the bauxite sample initially by sieving and then by treatment with 5 l of 0.5 mol/L HCl. Residual acid was washed from

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the bauxite and the organic material was then extracted for 24 h, under nitrogen, into 5 l of 0.5 mol/L NaOH. The aqueous extract was separated from the bauxite by centrifugation, acidified to pH 2, and left to stand for 3 days to precipitate the bauxite organic acid (BOC). The BOC was isolated by centrifugation and washed with three portions of 0.1 mol/L HCl. The remaining acidified extract, combined with the organic acid washings, was passed through a SPE column. The SPE procedure involved an ion-exchange cartridge, which was activated with 10 mL of 0.1 mol/L NaOH (percolation rate 3 mL /min). A 100-mL volume of BOC was passed through at a flow-rate of 0.5 mL/min. The cartridge was washed with 100 mL of water (3.0 mL/min) and organic acids were eluted with 50 mL of hydrochloric acid 0.1 mol/L (1.0 mL/min). This solution was injected directly in the chromatograph after filtered.

Chromatographic conditions

The mobile phases used were: A, 25 mmol/L potassium dihydrogenphosphate buffered at pH 2.10 with orthophosphoric acid; B, 100% methanol. All procedures were carried out using isocratic elution, with 11% methanol (B) in mobile phase A, filtered through a 0.45-μm membrane. The mobile phase was at a flow-rate of 1.30 mL/min. This mobile phase must be prepared fresh daily. The column was thermo stated at 25°C. Injection volume was 20 μL and all standards and Bauxite samples were injected in triplicate. The optimum wavelength for the simultaneous determination of the organic acids was 215 nm.

Calibration standards

The individual standards were dissolved in methanol and injected to determine individual retention times. Stock solutions of 1000 μg/mL of malonic acid, 2000 μg/mL of succinic acid, 200 μg/mL of oxalic acid, 5000 μg/mL of adipic acid, 5000μg/mL of glutaric acid, 2000 μg/mL of acetic acid, were prepared by dissolving pure standards into mobile phase. The stock solutions and the six diluted standards up to 10 times dilution from stock solutions were injected for linearity range and detection limit tests.

Results and discussions

Detection and quantification limits

The detection limit was calculated as $s_b + 3s$, where s_b is the average signal of ten blank injections and s the standard deviation. The quantification limit was calculated as $s_b + 10s$, where s_b is the average signal of ten blank injections and s the standard deviation. Table 1 showed the retention times of organic acids. Table 2 showed detection and quantification limits of organic acids analyzed. The detection limits ranged from 0.042 mg/L for oxalic acid to 10.36 mg/L for succinic acid and the quantification limits ranged from 0.67 mgLl for oxalic acid to 12.30 mg/L for succinic acid.

Calibration curves

Calibration curves were determined for seven different concentrations of a mixture of organic acids standard solutions. Each calibration sample was injected in triplicate. Calibration graphs for each compound were obtained by plotting concentration against peak area and applying the least squares method. Table 3 lists the parameters and correlation coefficients of the calibration plots. Each plot was linear over a wide interval from the detection limit to 250 μg/mL for malonic acid, 250 μg/mL for succinic acid, 25 μg/mL for oxalic acid, 500 μg/mL for adipic acid, 600 μg/mL for glutaric acid and 200 μg/mL for acetic acid. The peak areas (y) and the theoretical concentrations of the calibration standards (x) were fit to the ln-quadratic function using the least squares regression in Microsoft Excel. The results of the regression analysis were then used to back-calculate the concentration results from the peak area data, and the back-calculated concentrations and appropriate summary statistics [mean, standard deviation (SD), and percent relative standard deviation (RSD)] were calculated and presented in tabular form.

Precision

The precision study was comprised of repeatability and reproducibility studies. These were developed in five different Bauxites which contained low, medium and high

Table 1
RETENTION TIMES OF ORGANIC ACIDS ANALYZED

Organic acid	Retention time (min)±SD
oxalic	2.01±0.02
malonic	2.11±0.03
acetic	3.51±0.05
succinic	4.45±0.06
glutaric	5.63±0.05
adipic	7.68±0.07

Table 2
DETECTION AND QUANTIFICATION LIMITS OF ORGANIC ACIDS ANALYZED

Organic acid	Detection limit (mg/l)	Quantification limit (mg/l)
oxalic	0.042	0.067
malonic	2.02	3.43
acetic	1.47	1.86
succinic	10.36	12.30
glutaric	4.23	5.76
adipic	7.65	9.11

PARAMETERS AND CORRELATION COEFFICIENTS (*R*) OF CALIBRATION PLOTS FOR ANALYZED ORGANIC
ACIDS. CALIBRATION PLOTS ARE EXPRESSED AS REGRESSION LINES (*y=ax+b*),
WHERE *Y* IS THE PEAK AREA AND *X* IS THE AMOUNT OF ACID IN mg/L DETECTED LIQUOR.
THE CALIBRATION TEST WAS REPEATED THREE TIMES

Organic acid	a	b	r
oxalic	69.432	2.534	0.9991
malonic	11.014	4.325	0.9999
acetic	6.078	0.3613	0.9998
succinic	6.029	0.8927	0.9999
glutaric	7.272	0.7591	0.9999
adipic	7.526	0.9300	0.9998

Table 4
RECOVERY OF CARBOXYLIC ACIDS ADDED TO BAUXITES
AFTER SPE PROCEDURE

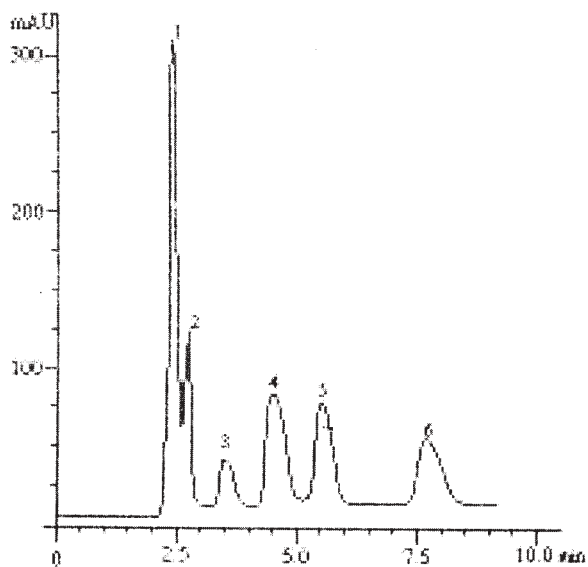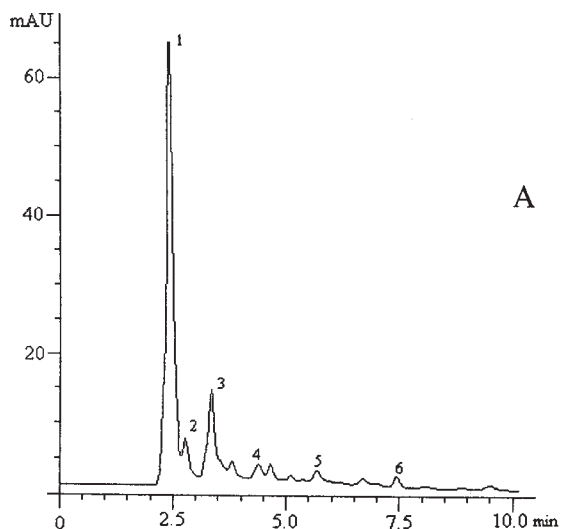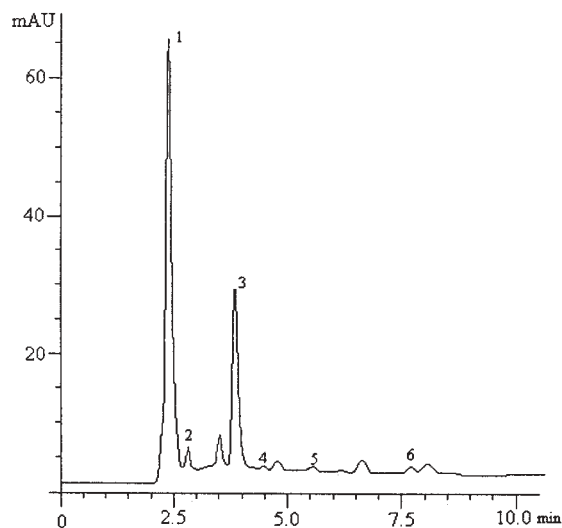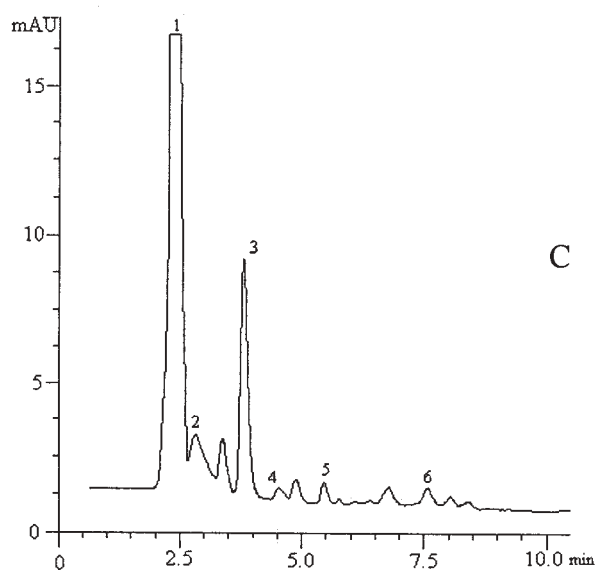| Organic acid	Recovery (%) (min)±SD	RSD (%)
oxalic	114.7±5.6	4.8
malonic	102.1±2.8	3.5
acetic	94.3±4.2	4.4
succinic	89.2±3.1	4.1
glutaric	106.1±7.3	6.9
adipic	93.9±2.9	3.1

Fig. 1. HPLC-UV chromatogram of the organic acid standards: oxalic
acid(1), malonic acid(2),
acetic acid(3), succinic acid(4), glutaric acid(5), adipic acid (6)

A

B

C

Fig. 2. HPLC-UV chromatogram of Bauxite samples: oxalic acid(1),
malonic acid(2), acetic acid(3), succinic acid(4), glutaric acid (5),
adipic acid (6). A, B, and C were bauxites of different origin (table 5)

organic acids levels. The repeatability was established by
injecting the samples five times. The reproducibility was
determined by analyzing each sample on 3 different days
over about 1 month. The relative standard deviations
(RSDs) of the repeatability and the reproducibility are
<2.13% and <3.24%, respectively. These results indicate
that the present method can be used for quantitative
analyses of organic acids in Bauxites.

Recovery
To establish the efficiency of the organic extraction, this
procedure was also performed on a mixture of organic

Origin	Oxalic/%	Malonic/%	Acetic/%	Succinic/%	Glutaric/%	Adipic/%
A	8.9×10^{-4}	7.7×10^{-4}	6.2×10^{-4}	2.0×10^{-4}	4.2×10^{-4}	2.2×10^{-4}
B	7.3×10^{-4}	6.1×10^{-4}	9.5×10^{-4}	1.1×10^{-5}	2.8×10^{-4}	8.5×10^{-5}
C	2.5×10^{-4}	1.8×10^{-4}	3.7×10^{-4}	1.0×10^{-6}	1.2×10^{-4}	2.0×10^{-5}

acids added to bauxite. Table 4 showed the recoveries of these carboxylic acids after applying the extraction procedure. It is not possible to compare to our results those of other researches because it is the first time that this study has been carried out to determine organic acids in Bauxites by high-performance liquid chromatography.

Organic acid content of Bauxite analyzed

The organic acid contents of five Bauxite samples are shown in table 5. It is the first time that these six oragnic acids have been determined and quantified in Bauxite samples. This variability could be explained by the different origin of the Bauxite. The oxalic and acetic acid concentrations were very high in all Bauxite sample. Figure 1 showed the typical chromatogram of standards of organic acids. Figure 2 showed chromatograms of Bauxite from Laos.

Conclusion
Chromatographic separations

A variety of techniques have been utilized for the identification and determination of sodium oxalate and organic substances in Bayer liquors; these have included titrimetry [7], ion chromatography [8-10], capillary electrophoresis [10-141, flow injection analysis [15], high performance liquid chromatograph[16-191 and gas chromatography [20-22]. However, only few reports focusing on identification and determination of other organic acids in Bayer liquors. But there were no reports for determination of organic acids in bauxite. Wilson separated humic substances from bauxite into seven fractions of different molecular weight and characterized by acidity, nuclear magnetic resonance (NMR) spectroscopy, infrared spectroscopy, pyrolysis gas chromatography mass spectrometry (py-GC/MS)21-22. Whelan et al /16-18] separated humics found in Bayer liquors on a Nova-Pak C18 column at a flow rate of 1.5mL/min using tetrabutylammonium hydrogen sulfate as the ion pairing reagent and a gradient was used. But the quantitative determination was not performance because the separation was not excellent. Oxalate was the main organic component in Bauxite. In many factories, the oxalate was determined by titration with standard potassium permanganate solution. This method often resulted in low precision and accuracy. Furthermore, it takes much time and agents.

Our particular interest concerns the development of a simple HPLC procedure for the determination of organic acids levels in Bauxite. It is the first time that high-performance liquid chromatography has been used to determine organic acids in Bauxite samples. A variety of techniques have been used for the determination of organic acids. In contrast to these methods, the present method is simple, rapid and requires only extraction steps.

First of all, working with standard solutions, six organic acids (oxalic, malonic, acetic, succinic, glutaric and adipic acid) were separated and identified by the present chromatographic method. Figure 1 showed a chromatogram of these organic acids standard solutions. The chromatogram of samples is showed in figure 2. A good separation can be achieved in a short separation time of 10 min.

In this study isocratic conditions were sufficient to separate six organic acids in a short time. Whelan et al16-18 separated humics found in Bayer liquors on a Nova-Pak C18 column at a flow rate of 1.5 mL/min using tetrabutylammonium hydrogen sulfate as the ion pairing reagent. A gradient was run using PIC A [5mM]/acetonitrile.

The levels of oxalate found in bauxite by RP-HPLC are in agreement with the volumetric analysis (VC): potassium permanganate titration. Deviation was 1.9%-3.7%. The oxalate levels determined by VC are always higher than the result of RP-HPLC. We conclude that potassium permanganate is a versatile and powerful oxidant that can be used to determine many substances by direct or indirect titration. Some other compounds in bauxite reacted with potassium permanganate.

Influence of mobile phase

Solutions of potassium dihydrogenphosphate buffered with orthophosphoric acid and sulphuric acid, recommended in the literature [23-25] for determination of organic acids, were used. Potassium dihydrogenphosphate buffered with orthophosphoric acid was selected because sulphuric acid produced interferences. Several concentrations of methanol (B) in mobile phase (A) were tested and finally 11% methanol (B) in mobile phase A was selected.

The analysis of organic acids in Bauxites with HPLC systems is a difficult task due to high ionic strength and pH. The present method allows the quantification of oxalic, malonic, acetic, succinic, glutaric and adipic acids in Bauxites. The present method has the advantage of measuring organic acid in a single run, thus simplifying the analytical procedure.

The analysis is simple, rapid and does not require any complicated sample preparation and only one reversed-phase column is used for the chromatographic separation in less than 10 min.

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