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Note

High-performance liquid chromatographic determination of humic acid in sodium aluminate solution[a]

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Humic acid is derived from plant matter and is present in soils. Bauxites can contain up to 0.6% of organic carbon, part of which is derived from humic acid. The Bayer process is the main industrial process for producing alumina (aluminium oxide) from bauxite ore. Bauxite is digested under pressure with hot sodium hydroxide solution to give a sodium aluminate solution. This is clarified and aluminium trihydroxide is precipitated by cooling and seeding. Aluminium trihydroxide is then calcined to produce alumina.

Organic matter, including humic acid, enters the process with the bauxite. With recycling of the liquor, the concentration of organics and their degradation products increases until an equilibrium concentration is reached. The presence of a significant amount of organic matter in Bayer liquor causes numerous process problems that include a lower alumina yield, generation of excessive fine aluminium trihydroxide particles, decreased alumina purity and colored liquor.

Attempts have been made to characterize and quantify the organics present in Bayer liquor[1,2]. Many components such as formic acid, acetic acid, propanetricarboxylic acid and benzenetetracarboxylic acid have been successfully measured by gas chromatographic–mass spectral analysis. The analysis of humic acid has been far less successful. Yet, a knowledge of humic acid concentration is important for monitoring and planning process control.

Recently a quantitative high-performance liquid chromatography (HPLC) assay for humic acid in environmental samples, including soils, was developed[3]. We decided to investigate its applicability to the analysis of humic acid in Bayer liquor. In this report we describe a new HPLC procedure with fluorometric detection. The method is simple and rapid, results for a single sample can be obtained within 10 min. Selectivity of this method is superior to that obtained by visible absorption measurement, an in-house method sometimes used.

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EXPERIMENTAL

The HPLC system consisted of a Waters Assoc. (Milford, MA, U.S.A.) M6000 pump and U6K injector, a Schoeffel (Westwood, NJ, U.S.A.) FS970 fluorometer and a Hewlett-Packard (Palo Alto, CA, U.S.A.) 3392A computing integrator. A Hitachi (Tokyo, Japan) F-4000 fluorescence spectrophotometer was used to scan HPLC-purified humic acids by using the flow cell attachment. Wherever possible, PTFE capillary tubing obtained from SGE (Ringwood, Australia) was used for the chromatographic lines. An SGE ODS 5-μm, glass-lined (250 × 4 mm I.D.) analytical column (plus guard column) was used for the chromatographic separation.

The mobile phase was prepared by mixing analytical-reagent grade ammonia purchased from Ajax Chemicals (Auburn, Australia) with Super-Q water prepared with a Millipore (Bedford, MA, U.S.A.) purification system. The ammonia concentration was 0.003% (w/v). The mobile phase flow-rate was 1 ml/min.

Technical-grade humic acid (sodium salt) was purchased from Aldrich (Gillingham, U.K.) and purified by dissolving in ammonia solution (pH 8), decanting and precipitating with Aristar-grade concentrated hydrochloric acid purchased from BDH (Poole, U.K.). The precipitate was filtered, air-dried at 22°C for 24 h and heat-dried at 80°C for 16 h. The procedure was repeated twice.

HPLC-purified humic acid that remained in the flow cell after diversion of the mobile phase was scanned for fluorescence excitation (240–380 nm; emission 440 nm) and emission (400–600 nm; excitation 340 nm). Since the retention times of the Aldrich and Bayer liquor humic acids and their fluorescence excitation and emission spectra were almost identical, purified Aldrich humic acid was considered to be a suitable standard.

Analytical-reagent grade sodium chloride purchased from Ajax Chemicals was heated at 550°C for 16 h to remove humic acid impurities. Bayer liquor samples were diluted 2000-fold in 0.5 *M* sodium chloride solution. An aliquot of 50 μl was injected into the HPLC system.

Humic acid fluorescence was detected at >418 nm with an excitation wavelength of 340 nm. Visible absorbance measurements were performed at 691 nm with a Pye-Unicam (Cambridge, U.K.) PU8600 absorbance spectrophotometer.

To quantify the humic acid concentration of Bayer liquor, a standard addition curve was constructed by spiking 500 μl of the diluted Bayer liquor with purified Aldrich humic acid (0.20–0.95 μg). Linear regression analysis confirmed the suitability of this technique ($r^2 = 0.998$).

RESULTS AND DISCUSSION

Prior to the development of an HPLC method, the fluorescence excitation and emission spectra and absorbance spectra of unchromatographed Bayer liquor and Aldrich humic acid were compared. Below about 500 nm the absorbance spectra were very different, obviously reflecting the mixture of organic components in Bayer liquor. Above this wavelength the spectra were similar (Fig. 1). Absorbance measurements of 19 Bayer liquor samples (measured at 691 nm) were compared with results obtained by HPLC. The correlation obtained by linear regression analysis was poor ($r^2 = 0.33$). This indicates that even at this wavelength visible absorbance is a poor analytical

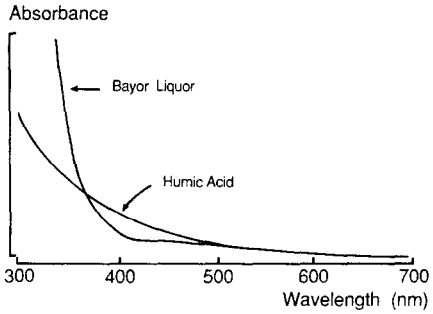

Fig. 1. Absorbance spectra of a purified Aldrich humic acid and a spent Bayer liquor.

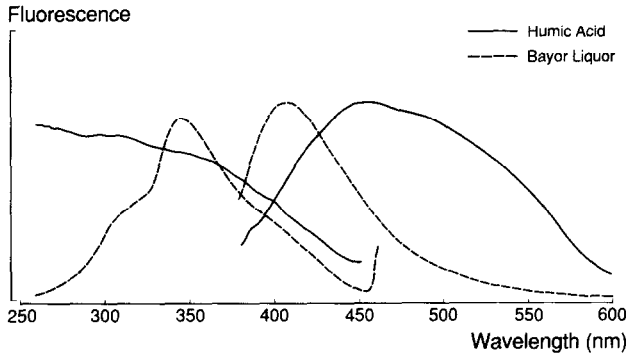

Fig. 2. Fluorescence spectra of a purified Aldrich humic acid and a spent Bayer liquor.

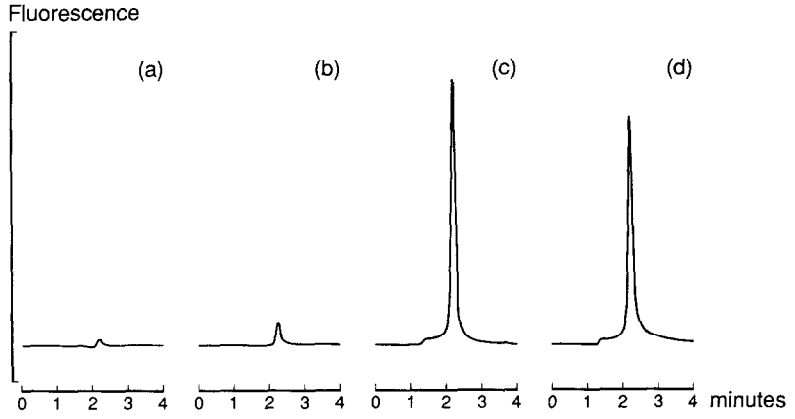

Fig. 3. Typical HPLC traces: (a) solvent blank; (b) Bayer liquor prior to extraction (0.23% humic acid); (c) Bayer liquor after extraction (3.51% humic acid); (d) standard humic acid (1.71 μg injected).

method due to the presence of a complex mixture of organics. Both the fluorescence excitation and emission spectra of the unchromatographed Bayer liquor were very different to the Aldrich humic acid (Fig. 2). Hence fluorescence measurements without chromatography were not further investigated as an analytical technique.

HPLC chromatograms were similar to those obtained in a previous study[3]. Typical chromatograms are shown in Fig. 3. The fluorescence ratio for excitation at 340 nm relative to 270 nm was 0.26 for both Aldrich humic acid and a plant liquor sample, indicating the absence of interfering components. We investigated the suitability of peak height measurement for quantification. Varying volumes of diluted Bayer liquor were injected. Linear regression analysis confirmed the suitability of peak height measurement for injection volumes between 10 μl and 75 μl ($r^2 = 0.998$). This enables a simple, low-cost HPLC system to be used for routine quality control monitoring. We chose an injection volume of 50 μl so that peak height measurement could be used without sacrificing accuracy. The relative standard deviation was 0.83% ($n = 10$). The limit of detection was 15 ng (2 $\times$ noise).

We found that humic acid comprised up to 5.27% (w/v) of a spent Bayer liquor. Such high levels underscore the desirability of having access to a rapid yet accurate analytical technique, given the many process problems encountered due to the presence of humic acid and its degradation products. This is the first report of a quantitative humic acid analysis of Bayer liquor by HPLC. The technique should prove to be a boon to process and production control in the alumina industry.

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