Cleaning Chemistry with Complexing Agents (CA): Direct Concentration Measurement of CAs with HPLC

S. Metzger and B.O. Kolbesen
Institute of Inorganic Chemistry, Johann Wolfgang Goethe-Universität
Marie-Curie-Str.11, D 60439 Frankfurt am Main, Germany
S.Metzger@chemie.uni-frankfurt.de, kolbesen@chemie.uni-frankfurt.de

Transition elements in semiconductor chemicals, although present in trace amounts, are a drawback in the cleaning of silicon surfaces. Apart from speeding up the degradation of the chemicals, particularly hydrogen peroxide, they are precipitated onto the wafer surface as metal hydroxides during the SC-1 cleaning procedure. One approach to preventing their precipitation is the addition of suitable complexing agents (CAs) to the SC-1 cleaning bath to bind and maintain them in solution for as long as is necessary. Stability in the alkaline SC-1 solution is an important criterion in the choice of CAs adopted and this may be determined by measuring their concentrations in an SC-1 bath over a given period of time.

High performance liquid chromatography (HPLC) being a well established method for the quantitative and qualitative determination of organic compounds was the method of choice but posed 2 problems:

- the difficulty of retaining ionic species on a reversed phase column, the standard column for HPLC.
- the possible damage to the silica-based column caused by the alkaline sample solution.

This paper presents a sample treatment developed for the separation of an ionic complexing agent on a reversed phase-C_{18} column.

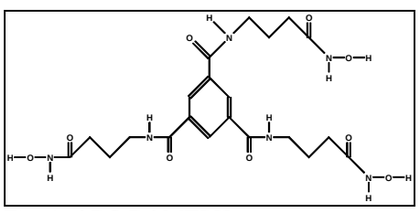

Fig. 1: ABS-BAMTPH

The hydroxamic acid complexing agent ABS-BAMTPH (Fig. 1) releases 3 hydrogen ions in neutral and alkaline solution. An acid needs to be added to the solvent in order to achieve retention. Fig. 2 shows the chromatograms of ABS-BAMTPH from an aqueous solution with a solvent mixture of water/acetonitrile containing also 0.1% trifluoroacetic acid (TFA). ABS-BAMTPH, synthesized in our group, also contained several by-products of the synthesis (Fig. 2, first chromatogram from the bottom.).

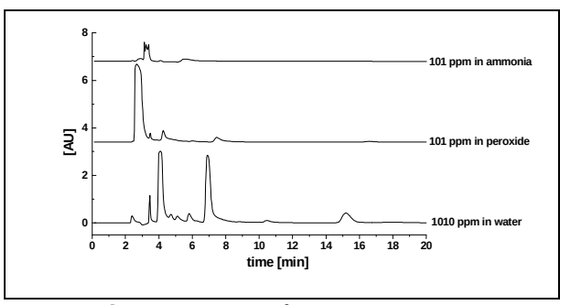

Fig. 2: Chromatograms of ABS-BAMTPH in water, peroxide and ammonia. Detection wavelength 220 nm.

The two components of SC-1 solution were tested separately to determine their specific influence on the retention. Hydrogen peroxide (Fig. 2, centre chromatogram) makes detection of any compound which elutes from 2.5 to 3.5 min retention impossible because of its strong UV absorbance due to its high concentration relative to the CA. The chromatogramm remains otherwise unchanged.
Ammonia posed the most problems as it kept the ABS-BAMTPH dissociated and altered the chromatogram completely (Fig. 2, uppermost chromatogram). The 0.1% TFA in the solvent was not sufficient to neutralize the 2.5% ammonia contained in the 100 µl sample injected. The ammonia also damaged the column permanently. A new column had to be used for subsequent measurements.

Several changes were necessary to achieve retention. The solvent was changed to a water/methanol gradient with 0.2% formic acid, this improved retention and the first peaks appeared after the peroxide peak. The detection wavelength was changed to 254 nm to reduce solvent absorption. Formic acid was added to the sample to neutralize the ammonia. The chromatogram of ABS-BAMTPH in water was taken as the reference for this method of separation.

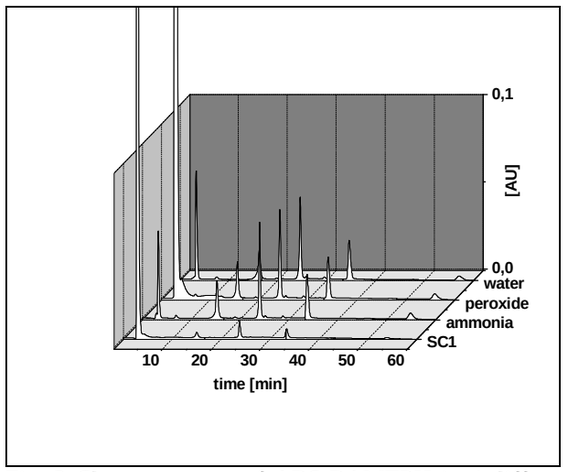

Fig. 3 Chromatograms of ABS-BAMTPH in 4 different matrices. Detection wavelength 254 nm. The large peroxide peak is not plotted completely in order to better show the 3 peaks of ABS-BAMTP.

With this method the 3 peaks of ABS-BAMPTH retained their positions when eluted from ammonia, hydrogen peroxide and SC-1as shown in Fig. 3. making the determination of CA concentration from all 3 matrices possible.

HPLC is a tool which can be used for the quantification of CAs from solution. Further applications are the detection and identification of decomposition products of CAs in order to understand the reactions involved.