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Ion-pair chromatography of bis (sodium-sulfopropyl) disulfide brightener in acidic copper plating baths

Roger Palmans [a,*], S. Claes [b], L.E. Vanatta [c], D.E. Coleman [d]

[a] *IMEC, Kapeldreef 75, B-3001 Leuven, Belgium*
[b] *Katholieke Hogeschool Leuven, Departement Rega, Sint-Maartensstraat 55d, B-3000 Leuven, Belgium*
[c] *Air Liquide - Balazs™ Analytical Services, Box 650311 MS 301, Dallas, TX 75265, USA*
[d] *Alcoa Technical Center, MST-C, 100 Technical Drive, Alcoa Center, PA 15069, USA*

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Abstract

Quantitative analysis of the brightener component bis (sodium-sulfopropyl) disulfide (SPS) in acidic copper plating baths poses a real challenge due to the complex chemical matrix containing large amounts of Cu(II) ion and sulfuric acid together with other organic additives and additive decomposition products. We developed a new ion-pair chromatography method to analyze micro-molar amounts of SPS directly in plating bath samples without the need for sample pre-treatment. Addition of tetra-*N*-methylammonium cation as ion-pairing agent to a methanol–sulfuric acid–water eluent increases the retention time of the anionic SPS^{2-} on a C_{18} column sufficiently to separate this compound from Cu(II) ion and additive by-products.

Keywords: Ion-pair chromatography; SPS; Bis (sodium-sulfopropyl) disulfide; 4,5-Dithiaoctane-1,8-disulfonic acid; 3-(Mercaptopropane) sulfonic acid; MPS; Brightener additive; Acidic copper plating bath; Regression statistics

1. Introduction

Electrolytic copper plating from sulfuric acid copper plating baths has become the method of choice for copper film deposition in dual damascene metallization schemes for chip production [1]. In this type of application, narrow trenches (horizontal interconnects) and vias (vertical interconnects) with widths typically below 100 nm and high aspect ratio geometries have to be reliably filled with high quality copper metal for on-wafer conductor wiring purposes. This poses stringent requirements on the copper plating bath composition, and frequent chemical analysis of the plating bath for both inorganic and organic components has to be performed. Current automated analysis methods for acidic copper plating baths are mainly based on a series of titrations for the inorganic components (Cl^-, H_2SO_4, Cu^{2+}), whereas cyclic voltammetric stripping (CVS) is used almost exclusively for analysis of the organic additives [1,2]. Current copper plating baths for on chip metallization contain at least two organic additives, a so-called brightener or accelerator compound, and a carrier or suppressor component. Especially the brightener compound has to be monitored on a frequent basis due to its decomposition, both during the copper electroplating process as well as during idle periods when the plating bath is circulated continuously over the copper anode in the plating tool [3]. A common brightener used in acidic copper plating baths is the compound 4,5-dithiaoctane-1,8-disulfonic acid (or its disodium salt), also known as bis (sodium-sulfopropyl) disulfide or bis (3-sulfopropyl) disulfide (disodium salt). This compound is best known under the acronym SPS, and will be referred to as such in this paper. The function of SPS is to promote the so-called bottom-up fill of narrow features on the wafer and to deposit a good quality copper film with acceptable roughness and grain growth capability. Although cyclic voltammetric stripping has found

* Corresponding author. Tel.: +32 16 281 459; fax: +32 16 281 214.
E-mail address: palmans@imec.be (R. Palmans).

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widespread acceptance for the analysis of organic additives in copper electroplating baths, several disadvantages of this electrochemical analysis technique have to be taken into account. Basically, cyclic voltammetric stripping is an indirect measurement technique that determines the combined electrochemical effect of the additives (not only from the active organic components, but also from some decomposition products, and chloride ion) on the amount of Cu deposited on a working electrode. Cyclic voltammetric stripping involves a lengthy procedure that can take up to several hours for the analysis of both SPS and the suppressor. Moreover, this analysis method is error-prone, and the analysis results become unreliable when the levels of the two additives are out of the normal working range. Also, cyclic voltammetric stripping becomes useless when too high levels of decomposition products have accumulated in the plating bath. Finally, cyclic voltammetric stripping does not provide information on the decomposition products that accumulate in the plating bath in the course of its lifetime. These decomposition products can affect the quality of the deposited copper film and the reliability of the filling of the narrowest features. Moreover, some decomposition products such as MPS (3-mercaptopropane) sulfonic acid, the monomeric thiol fragment originating from breaking of the disulfide bond of SPS, are expected to influence the cyclic voltammetric stripping measurement because they show similar electrochemically activity under the cyclic voltammetric conditions used in the analysis of SPS [3].

Due to the problems associated with the cyclic voltammetric stripping analysis technique, we were interested in the development of an alternative and more reliable and quantitative analysis method for SPS that would not suffer from the disadvantages of cyclic voltammetric stripping, and would provide us at the same time with information about decomposition product accumulation in the plating bath during extended periods of plating activity on a commercial plating tool. From literature accounts, only a few efforts have been described so far to apply HPLC chromatographic separation techniques for analysis of SPS in acidic copper electroplating baths [4–7]. The challenge for these chromatographic methods is to analyze SPS in the concentration range between about 10^{-5} and 10^{-4} M in a chemical matrix containing very high levels of both Cu(II) ion and sulfuric acid. An interesting alternative to HPLC was described by Shohat and Grushka [8]. They used ion-pair reversed-phase chromatography to retain the SPS anion more strongly on a C_{18} column. However, in their procedure, removal of the excess Cu(II) ion from the plating bath samples prior to injection in the chromatographic system was still required.

In this paper the development of an ion-pair chromatography method on a C_{18} reversed-phase column is presented for direct analysis of SPS in an acidic copper plating bath without the need for any pre-treatment of the samples. A full calibration study with statistical analysis was performed on the calibration data of SPS analyzed by the new ion-pair chromatography method. This information was used to follow-up the SPS concentration in a Shipley-Ronal Electraplate copper plating bath over an extensive time period. Furthermore, ion-pair chromatography analysis of these copper electroplating bath samples provided a fingerprint of some of the decomposition products that accumulate over time in the plating bath.

2. Experimental

2.1. Chromatographic set-up

All analyses were performed on a Dionex (Sunnyvale, CA, USA) DX-500 ion chromatographic system. The set-up consists of a GP50 gradient pump, an LC20 enclosure, and an AD20 absorption detector. Instrument control and data acquisition were handled by the Peaknet 5.1 software package installed on a personal computer. The column used for analytical separation was an Alltech (Alltech Associates, Inc., Deerfield, USA) reversed-phase Prevail C_{18} (150 mm × 3.2 mm) coupled to an Alltech guard column (7.5 mm × 4.6 mm). This column was chosen because of its compatibility with the highly acidic conditions encountered with copper plating bath samples. All separations were conducted in isocratic elution mode (0.7 mL/min) at room temperature without temperature control of the column. The sample loop volume amounted to 25 μL. For standard HPLC analyses, Dionex OnGuard II-H cartridges were employed to remove Cu(II) ion from the samples before injection.

2.2. Chemicals and samples

Pro Analysis grade chemicals were used throughout this study whenever available. Spectrophotometric grade methanol was obtained from Sigma-Aldrich (Bornem, Belgium). Tetra-*N*-methylammonium chloride (98 + % purity) was obtained from Alfa Aesar, Johnson Matthey (Karlsruhe, Germany). Sulfuric acid 0.5 M standardized solution and $CuSO_4{\cdot}5H_2O$ p.a. were obtained from VWR (Leuven, Belgium). The active brightener component SPS was a kind gift from Raschig GmbH (Germany). The purity of this compound was not specified but it proved to contain some MPS. The SPS-decomposition product MPS (∼80% specified purity, technical grade) was obtained from Fluka (Bornem, Belgium). Based on an ion-pair chromatographic calibration graph for MPS, the concentration of MPS in the SPS product was determined to be 0.022% (w/w). Other minor impurities present in the SPS product were Cl^- and SO_4^{2-} ion which amounted together to less than 0.5 % (w/w) as determined by ion-chromatography analysis. High purity deionized water with a specific resistivity of 18.2 MΩ cm (0.055 μS cm^{-1}) was provided by the IMEC Pline cleanroom purification system, and was used to prepare all eluents and standard solutions. Copper plating bath samples were obtained from an Applied Materials Electra iECP™ plating tool using the Shipley-Ronal Electraplate two-additive chemistry (with brightener Additive-X and suppressor Additive-Y). The tank

volume was 200 L and the plating bath was continuously recirculated through a 0.2 micron filter unit. The plating bath temperature is controlled at 15 °C. Plating bath samples were collected in PE vials via an external sampling port on the CDU that was connected to the main plating bath tank, and injected after temperature equilibration by means of a syringe into the injection port of the chromatographic system without filtration or any other pre-treatment step.

2.3. Calibration procedure

Calibration of SPS by ion-pair chromatography was performed in the relevant concentration range between 1.4×10^{-5} and 1.41×10^{-4} M. However, it was established that the linear response range for the calibration graph extended to 1.7×10^{-3} M. Higher SPS levels were not evaluated in this study. The lowest SPS level observed in the plating bath was situated around 1.7×10^{-5} M. As a consequence, it was deemed unnecessary for this study to extend to calibration graph below the 1.4×10^{-5} M level, which is already far below the SPS concentration recommended for obtaining good quality copper filling with Shipley-Ronal Electraplate plating bath [2]. The calibration study involved 8 SPS concentration levels and 9 replicates. The calibration design was chosen in such a way that evenly spaced concentration levels were present in the range between 1.4×10^{-5} and 8.5×10^{-5} M. The design was completed with the 1.13×10^{-4} and 1.41×10^{-4} M levels. For each replicate analysis of these calibration standards, a new stock solution of SPS in water was prepared in order to avoid any decomposition of the compound over the long time that this study took, and to include all possible error sources during preparation of the calibration solutions. The concentrations of SPS were kept as close as possible to the nominal values, but were not exact for each replicate due to difficulty in weighing small amounts of SPS. For each calibration solution, two repeat injections were done, and the average of the measured peak area values was used as the response at each concentration level and for each replicate. Statistical evaluation was performed with the statistical software package JMP 5.1 (SAS Institute, Inc., Cary, NC, USA).

3. Results and discussion

3.1. Method development

Due to the strongly ionic nature of SPS^{2-} [9], this anion is almost not retained when eluted over reversed-phase C_{18} column using a methanol–water–sulfuric acid eluent. Even in such a low pH eluent, this anion is fully dissociated in solution and no retention mechanism with a C_{18} column is available. As a consequence, SPS in acidic copper plating bath samples is found to elute with almost the same retention time as the large excess of Cu(II) ions. This is exemplified in Fig. 1 which shows overlay chromatograms of Cu(II) ion in water (2 g/L) and SPS in water (2.8×10^{-4} M) eluted over an Alltech Prevail C_{18} column with an acidic methanol–water eluent (70% MeOH–30% H_2O with 0.005 M H_2SO_4) mobile phase with UV absorption detection at a wavelength of 205 nm. Clearly, the SPS peak elutes at almost the same time as the fast eluting Cu(II) ion. As a consequence, analysis of SPS in copper plating bath samples by standard HPLC methods over a C_{18} type column requires the removal of the excess Cu(II) ions by means of e.g. solid phase extraction (SPE) prior to injection in the chromatographic system. However, due to the extremely high level of Cu(II) ion encountered in acidic copper plating baths, the bath samples have to be diluted before SPE treatment, requiring several Cu-specific SPE cartridges for each sample due to their limited capacity. The result of a standard HPLC analysis of a production copper plating bath sample is presented in Fig. 2. In this example, the sample had to be diluted ten times before SPE removal of Cu(II) ion.

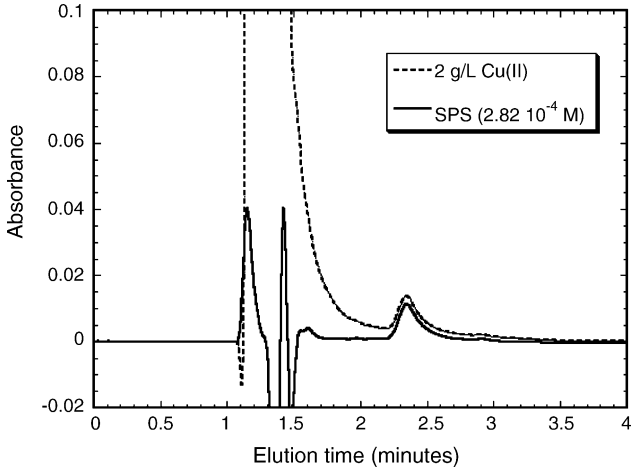

Fig. 1. Overlay chromatograms of Cu(II) ion (2 g/L) and SPS (2.8×10^{-4} M) after elution over Alltech Prevail C_{18} column with an eluent containing 70% (v/v) methanol and 30% (v/v) DI water with 0.005 M sulfuric acid.

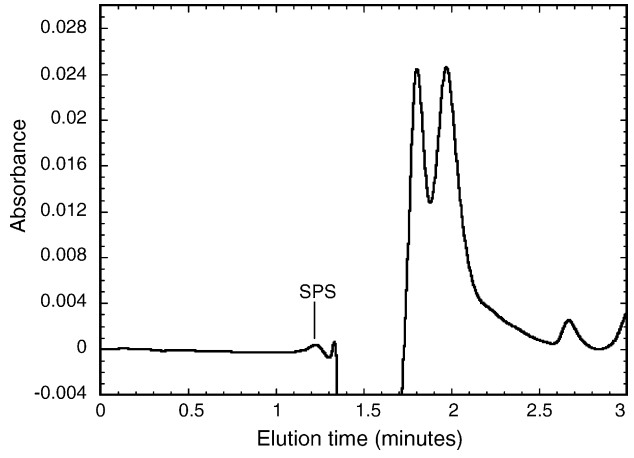

Fig. 2. HPLC chromatogram of a Shipley-Ronal Electraplate production plating bath sample (10× diluted) after copper removal by SPE. Altech Prevail C_{18} column, 86.4% (v/v) methanol and 13.6% (v/v) DI water with 0.02 M sulfuric acid.

Although the SPE was able to remove all interfering Cu(II) ions, this type of analysis proved unsatisfactory because of detection limit problems. Indeed, the resulting SPS peak at $t_R \sim 1.25$ min was barely discernable above the background signal. As a consequence, SPS analysis in copper plating bath samples by standard HPLC methodology was deemed unsuitable due to the need for a time-consuming and costly pre-treatment procedure for the plating bath samples. Consequently, an improved and more sensitive chromatographic analysis method is required for direct analysis of the SPS brightener additive in acidic copper plating baths.

Based on the findings of Shohat and Grushka [8], it was known that addition of a bulky hydrophobic ion-pairing agent such as the tetra-*N*-butylammonium cation to the mobile phase resulted in an improved retention of the highly ionic SPS^{2-} on a standard C_{18} type column. Consequently, we have investigated the elution behavior of the SPS^{2-} anion on an acid compatible Alltech Prevail C_{18} column when an oppositely charged ion-pairing agent such as a quarternary ammonium cation is added to the eluent. The goal was to sufficiently retard the elution of anionic SPS^{2-} species (and other anionic species present in the plating bath samples) with respect to the large excess of fast eluting Cu(II) ion in order to make quantitative analysis feasible. Preliminary experiments with addition of tetra-*N*-methylammonium chloride (TMAC) to an eluent composed of methanol–water–sulfuric acid showed that SPS^{2-} is indeed retained on the C_{18} column. This was tested with a genuine sample of SPS dissolved in water and eluted with an eluent with the composition 20% (v/v) methanol–0.02 M H_2SO_4–40 mM TMAC in DI water. Fig. 3 shows the chromatograms of a sample of 1.14×10^{-3} M SPS in water eluted with both an optimized standard HPLC eluent containing methanol–sulfuric acid–water and the new ion-pair chromatography eluent with the addition of TMAC. A first observation is that the peak attributed to SPS has shifted considerably to longer retention time under the ion-pair chromatography elution conditions, and secondly, the peak shape for SPS has improved substantially as compared to the standard HPLC chromatogram of the same sample. Further optimization of the eluent composition in view of SPS peak retention time was performed in order to obtain the best possible detection of SPS in real plating bath samples where SPS needs to be separated from the large amount of Cu(II) ion. The influence of the eluent composition on the retention time of SPS was studied by changing the concentrations of the different eluent components over suitable concentration ranges while maintaining the other components at a constant concentration. Fig. 4 shows the influence of the concentration of the organic solvent in the eluent mixture. These test were performed with mobile phases containing 0.02 M sulfuric acid and 40 mM of TMAC in water whereas the methanol concentration was varied between 3 and 30% (v/v). The concentration of methanol has a pronounced effect on the SPS peak retention time, with higher methanol concentrations resulting in shorter retention times for SPS. Under the conditions used, t_R of SPS ranges from about 2–20 min. The peak shape becomes more symmetrical for the shorter retention times. The SPS peak positions turn out to be inversely proportional to the methanol concentration. In contrast to the effect of methanol on the SPS retention time, neither sulfuric acid nor TMAC showed any pronounced effect on the peak position of SPS when the other components in the eluent were kept at constant concentration (figures not included). A range in t_R for SPS of less than 1.5 min was observed for sulfuric acid levels between 0 and 0.025 M, or when the TMAC concentration was varied between 30 and 50 mM. For these tests, the methanol concentration was kept at 5% (v/v). The retention behavior of SPS for different methanol concentrations in the mobile phase could be indicative of the elution of neutral ion-pairs formed between $(CH_3)_4N^+$-ions and SPS^{2-} that are

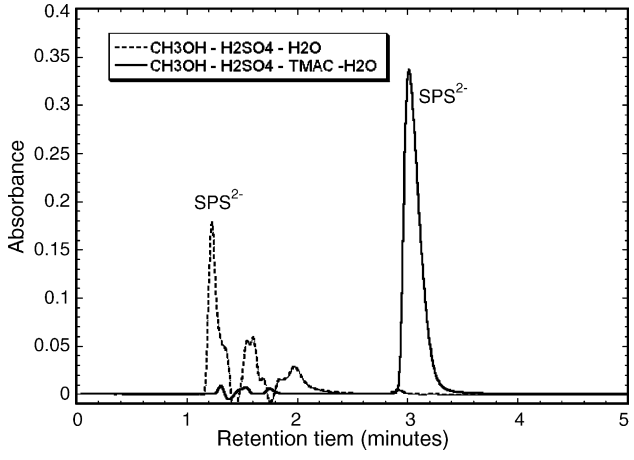

Fig. 3. Overlay chromatograms of SPS (1.14×10^{-3} M in DI water) obtained by (1) HPLC over an Altech Prevail C_{18} column with a 86.4% (v/v) methanol and 13.6% (v/v) DI water with 0.02 M sulfuric acid eluent (dotted trace) and (2) by ion-pair chromatography over the same column using a 20% (v/v) methanol and 80% (v/v) DI water with 0.02 M sulfuric acid and 40 mM of TMAC as ion-pairing agent.

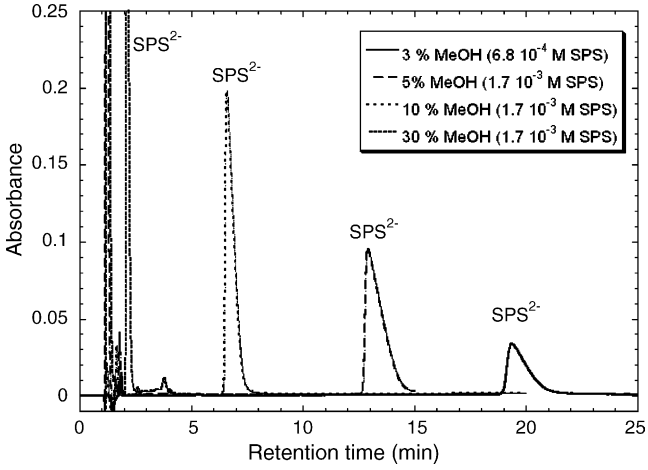

Fig. 4. Influence of the methanol concentration in the ion-pair chromatography eluent mixture on the retention behavior of SPS over an Alltech Prevail C_{18} column. Conditions: methanol concentrations of 3, 5, 10 or 30% (v/v) with 0.02 M of sulfuric acid and 40 mM of TMAC as ion-pairing agent.

more strongly retained on the C_{18} column than the charged SPS^{2-} anion. When the organic content of the mobile phase is increased, the retention time is expected to decrease due to a more favorable distribution of SPS in the mobile phase. The fact that the concentration of TMAC does not play a major role in the retention behavior of SPS indicates that a minimum amount of the ion-pairing agent is sufficient to induce the retardation effect, and that, once the ion pairs have been formed, addition of excess ion-pairing agent does not lead to any further retardation. Another possible retention mechanism involving derivatization of the column packing material with the quarternary ammonium group is less likely because the retention behavior observed when the methanol concentration is varied in the eluent mixture is not compatible with the expected ion-exchange mechanism whereby anionic SPS would interact with the derivatized column material.

No major sensitivity effects for the peak area of SPS were observed between the different eluent compositions during this study. As a consequence, the final choice of the eluent for the ion-pair chromatography method was only determined by the required shift in peak position of SPS compared to the Cu(II) ion peak and to peaks due to decomposition products present in plating bath samples. Fig. 5 shows a typical ion-pair chromatography chromatogram for an actual production plating bath sample obtained during the normal working lifetime of the plating bath. For comparison purposes, the chromatogram of a freshly prepared plating bath sample is included. These chromatograms, obtained with the optimized eluent containing 5% (v/v) methanol, 0.02 M sulfuric acid, and 40 mM TMAC, show excellent separation of SPS^{2-} ($t_R \sim 14.4$ min) from a series of other compounds detected at 205 nm by UV absorbance measurement, and from the excess Cu(II) ion that elutes immediately after the void and prior to the other components. The plating bath sample was injected directly into the injection port of the chromatographic set-up

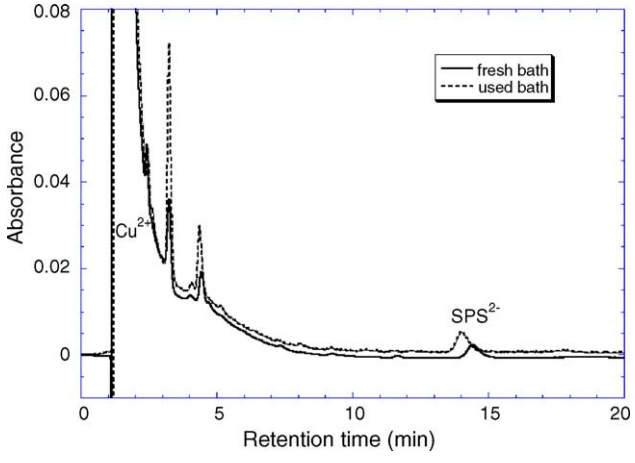

Fig. 5. Ion-pair chromatography chromatogram of a production sample of the Shipley-Ronal electraplate bath compared to a freshly prepared plating bath. Conditions: Alltech Prevail C_{18} column with 5% (v/v) methanol–0.02 M sulfuric acid–40 mM TMAC eluent. Flow rate 0.7 mL/min.

without any pre-treatment. The new ion-pair chromatography method for SPS allows a complete analysis in about 15 min for copper plating bath samples. Moreover, the method is sufficiently sensitive to detect the expected low levels of SPS present in actual plating bath samples (see further). A freshly prepared plating bath sample shows, except for the SPS and Cu(II) ion related peaks, two other major peaks (t_R 3.24 and 4.44 min) and some minor peaks (t_R 4.05, 4.74, 5.20, 7.42, 9.28, and 11.7 min). These peaks are suspected to be due to either impurities or decomposition products of the additives present in the plating bath. Currently, no information is available about the nature of these compounds. During the normal working lifetime of the plating bath, the major change observed in the ion-pair chromatograms of copper plating bath samples is an increase in intensity of the two major peaks (t_R 3.24 and 4.44 min) together with a slight increase in peak height of the bands at 4.05 and 5.13 min. Two new peaks at retention times of respectively 2.65 (shoulder on the Cu(II) ion peak) and 8.07 min are found after several months of use of the plating bath pointing the accumulation of some new decomposition products in the plating bath.

One issue that remains to be solved with the current ion-pair chromatography method is a slow shift to shorter times of the SPS retention time over working periods of several months. This effect is believed to be due to the influence of sulfuric acid on column behavior. Although the Alltech Prevail C_{18} column should be compatible with the acidic conditions present in the plating bath samples and the mobile phase used in this study, some modification of the column packing material seems to happen over extensive periods of time. However, these shifts in retention time do not affect the sensitivity of the measurement method. No major changes in peak area values were observed although the retention time shifted from almost 14 min to about 10.5 min after several months of use of the same column. Also, this effect is observed to a lesser extent for the by-product peaks, thus still allowing to follow-up the by-product build-up.

3.2. SPS calibration diagnostics

In order to obtain meaningful statistical information about the ion-pair chromatography analysis method for SPS, an extensive calibration study was performed. The calibration procedure used in this study was described in the experimental section. A calibration design with 8 concentration levels between 1.4×10^{-5} and 1.4×10^{-4} M, and 9 replicate calibration curves was performed over a period of about 2 months. In the design all possible handling errors are taken into account, also the variations in the actual SPS weighed for each calibration stock solution.

In determining an appropriate model and fitting technique for a set of calibration data, the first step is to investigate the behavior of the standard deviation of the responses (i.e., peak areas). However, this procedure requires that the replicate measurements at each concentration be of exact concentration replicates. In this research, such standards are not avail-

able, although each concentration is known exactly (i.e., with small uncertainty). Therefore, a modified statistical strategy was devised and implemented, as described below.

First, each group of concentrations had to be evaluated to determine if the peak areas trended upwards as the concentration values increased. If such a phenomenon were found to be the case, then the spread of the concentrations would be too wide to be considered to be one level. To make this determination, the data were grouped by target concentration (i.e., 1.4×10^{-5}, 2.8×10^{-5}, 4.2×10^{-5}, 5.6×10^{-5}, 7.1×10^{-5}, 8.5×10^{-5}, 1.13×10^{-4}, and 1.41×10^{-4} M). Within each group, the actual peak areas were plotted versus the actual concentrations. Each set of data was fitted with a straight line, using ordinary least squares as the fitting technique. If the *p*-value for the slope of any line were found to be significant (i.e., less than 1%), then an upward trend in the peak area was deemed to exist. However, at all concentrations, the *p*-value was well above the cut-off value of 1% (the actual *p*-values ranged from 0.2210 to 0.7654). Thus, it was appropriate to consider each set of concentrations as a defined group for purposes of modeling the standard deviation.

The second step was to determine an appropriate concentration value to represent each group. The mean is such a statistic and was chosen here.

Third, the peak areas were scaled to each mean. Although there was no upward trend of peak areas within each group, the overall trend was upward as concentration levels increased (as is expected for calibration data). To determine an appropriate scaling factor, the raw data were fitted with a straight line, using OLS (i.e., with a reasonable first-order approximation curve). The slope of this line was used to scale each measured peak area to its respective mean.

Fourth, the standard deviation of the peak areas was modeled by grouping the data by mean concentration, and then determining the standard deviation of the scaled peak areas for each group. A Straight-Line/OLS model/fit of these data showed that the *p*-value for the slope was 0.0006, well below the 1% cut-off value. Thus, the standard deviation was seen to be changing with concentration, meaning that WLS was needed. Weights were calculated using the equation for this straight-line fit [10].

Once the appropriate fitting technique (WLS) had been selected, the proposed straight-line model could be tested; the above-calculated weights were used in the regression of the raw peak area data versus true concentrations. The traditional lack-of-fit test (LOF) was not available for these data, again because of the inexactness of the replicates. The first alternative approach was to rely on evaluation of residual patterns. If the residuals for the proposed calibration curve are plotted versus the target concentrations, the mean of each group should fall approximately on the zero line; otherwise, at least one term is lacking from the model [11]. As can be seen in Fig. 6, this phenomenon appeared to be the case with these data. A second alternative approach allowed the use of a formal LOF test. Although the original data were used (and should be used) for the WLS that provided final calibration

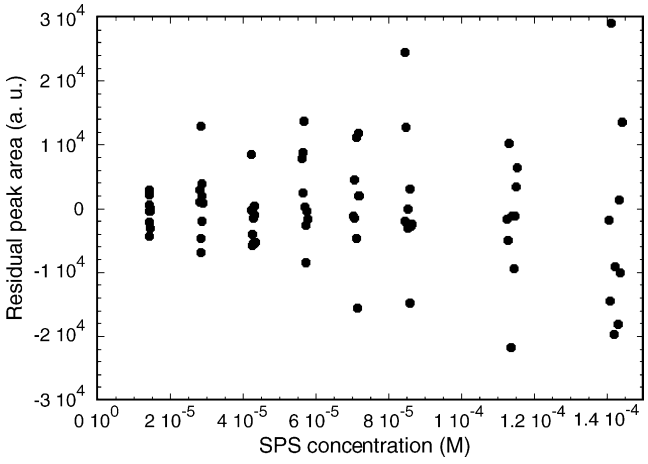

Fig. 6. Residuals plot for straight-line regression of raw peak area data versus true SPS concentration.

coefficients, an additional SL/WLS curve was constructed with the scaled peak area data. This second plot was used solely for the purpose of performing a lack-of-fit test (the coefficients were not used). The *p*-value for this test was 0.7269, indicating that there was no evidence of lack of fit with the SL model [12]. While this is not an exact *p*-value (due to the use of scaled data), there were two reasons to be confident in the decision: (1) the relative variation within each set of standards was small compared to the range of concentrations in the standards; (2) the *p*-value was much greater than any threshold that would be considered for determining statistical significance.

In step 3, the scaling process was conducted by assuming that a SL/OLS model/fit was a reasonable combination for these peak area data. The above paragraph has shown that the SL assumption was correct. However, since WLS was found to be the appropriate fitting technique, the scaling process technically should be carried out using WLS. This iteration was performed; the new weights were different from the first ones by no more than 0.0027, an amount considered to be insignificant.

A final check on the adequacy of a straight-line fit was made by fitting a quadratic to the data, again using WLS. The *p*-value for the quadratic term was 0.2768, meaning that this term was insignificant and therefore over-fitting the data. Thus, a straight-line with WLS fitting was chosen as an adequate model for these data. A plot of the curve, along with the upper and lower 95% prediction intervals, is presented in Fig. 7.

3.3. Ion-pair chromatography follow-up of SPS in a production copper plating bath

Based on the calibration graph obtained in the previous section, the ion-pair chromatography method was first used to determine the SPS concentration in the stock solution of the brightener additive (Add-X) after adequate dilution to bring the resulting SPS concentration within the range of

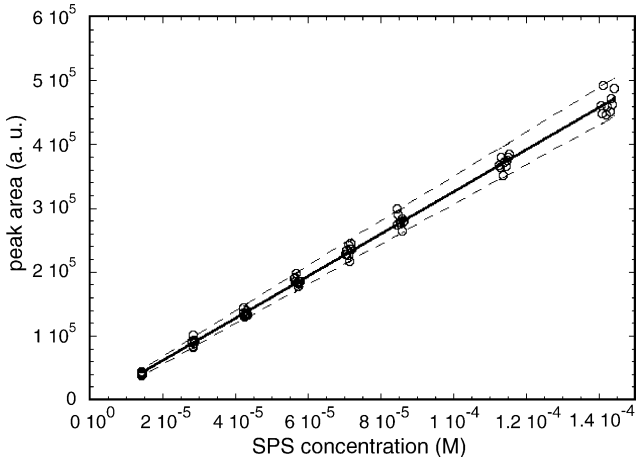

Fig. 7. Calibration graph (solid line) for SPS with straight-line regression (using weighted least squares) of raw peak area data versus true SPS concentrations. Also shown are the upper and lower prediction intervals (at 95% confidence; dotted lines).

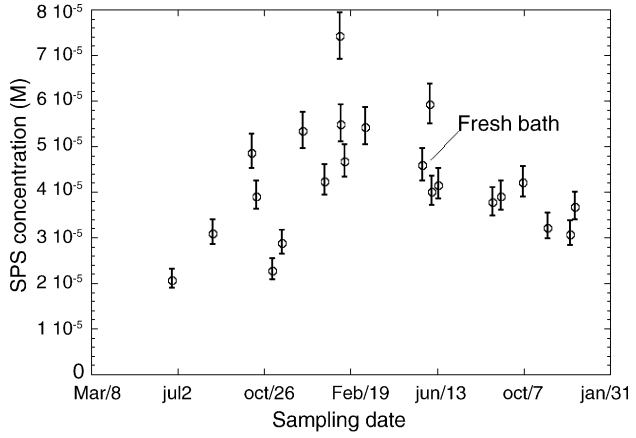

Fig. 8. Follow-up of the SPS concentration in a production plating bath (Shipley-Ronal Electraplate) over an extensive working period by ion-pair chromatography. Ion-pair chromatography conditions: Alltech Prevail C_{18} column with 5% (v/v) methanol–0.02 M sulfuric acid–40 mM TMAC eluent. Flow rate 0.7 mL/min.

the calibration graph. From this measurement, the starting level of SPS in a freshly made plating bath was calculated to be around 5.6×10^{-5} M (taking into account the dilution of the brightener stock solution during the plating bath make-up procedure). As a consequence, this SPS concentration in the plating bath is expected to be maintained within some preset limits by the automated cyclic voltammetric stripping measurement and subsequent automatic replenishment. As a consequence, most plating bath samples were expected to be within the targeted SPS range according to cyclic voltammetric stripping analysis. Because the sampling of the plating bath was done within 4 h of the cyclic voltammetric stripping measurement for the brightener additive, the level of SPS should be close to the SPS level set after cyclic voltammetric stripping measurement and brightener addition to the plating bath. However, when the actual SPS concentrations were followed-up over an extensive working period, both very low and very high levels of SPS were measured, as can be inferred from Fig. 8. Only in the case of the 7.3×10^{-5} M SPS level data point, it was known that too much brightener additive had been added to the plating bath by mistake, and this fact was indeed detected by the ion-pair chromatography analysis. These first results indicate that SPS levels in this plating bath were varying over a much wider range than expected. Clearly, the standard cyclic voltammetric stripping measurement method did not detect these variations, indicating that other components present in the plating bath do indeed influence the cyclic voltammetric stripping results for SPS measurement.

Ion-pair chromatography was also used to follow-up the build-up of additive decomposition products over the lifetime of a plating bath. Typical changes in the chromatograms of plating bath samples during the normal working lifetime of the plating bath were already discussed earlier (Fig. 5). Typical changes in the chromatograms over time involve the increase in intensity of two major peaks (t_R 3.24 and 4.44 min) whereas only some minor changes are observed in other peaks.

Interestingly, when the plating bath is used beyond its normal working lifetime (as recommended by the vendor), progressively more peaks due to new anionic decomposition products appear in the plating bath sample chromatograms. This is exemplified in Fig. 9 where a comparison is made between two ion-pair chromatography chromatograms obtained from respectively a fresh and an exhaustively used plating bath (this bath was used substantially longer than the recommended lifetime expectancy as defined by the vendor). A whole range of new anionic decomposition products can be detected by ion-pair chromatography after extensive use of the plating bath as is evidenced by the appearance of five new peaks in the chromatograms of the overused plating bath

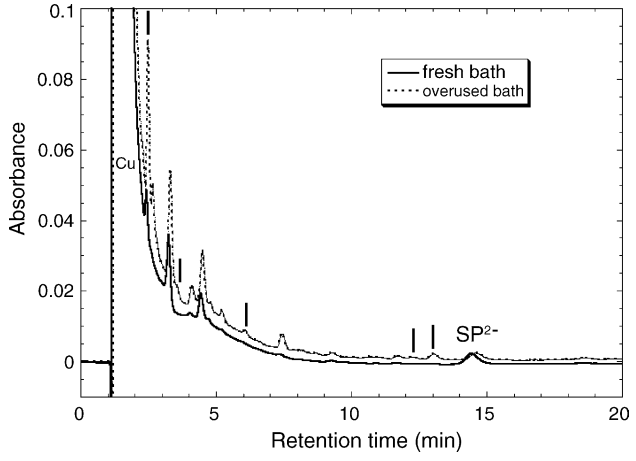

Fig. 9. Comparison of the ion-pair chromatography chromatograms of an exhaustively used production plating bath and a freshly prepared plating bath. Major new peaks in the chromatogram of the overused plating bath are indicated with vertical markers. Ion-pair chromatography conditions: Alltech Prevail C_{18} column with 5% (v/v) methanol–0.02 M sulfuric acid–40 mM TMAC eluent. Flow rate 0.7 mL/min.

sample. For clarity these new peaks have been labeled with vertical markers (retention times of 2.48, 3.50 (sh), 6.06, 12.19, and 13.00 min). The latter peaks are not detected to any extent during the normal working lifetime of the plating bath (Fig. 5). Especially the appearance of the intense peak with a retention time of 2.48 min could, in principle, be used as a decision point to replace the plating bath before too many by-products accumulate which are expected to have a detrimental effect on the quality of the plated copper film and the copper filling characteristics. Consequently, ion-pair chromatography can be used to obtain a fingerprint of the accumulation of decomposition products during the lifetime of a plating bath. So far, no assignation of the unknown peaks in the chromatogram has been attempted. This would require, e.g. the coupling of the chromatographic method with a technique such as mass spectrometry.

Contrary to expectations, none of the peaks observed in the ion-pair chromatograms of copper plating bath samples could be assigned to 3-(mercaptopropane) sulfonic acid (MPS), a suspected thiol decomposition product of SPS brightener molecule, because the typical peak of MPS with a retention time of 3.73 min could not be detected in the plating bath samples even after extensive use. The reason for the absence of MPS (at least to a detectable level) was found to be due to the quantitative conversion of MPS to SPS in aqueous solution in the presence of Cu(II) ions. This reaction occurs as well in the presence as in the absence of sulfuric acid. This hitherto unknown reaction was proved by the ion-chromatography method when an MPS sample in aqueous solution was mixed with Cu(II) ions. In the absence of Cu(II) ions, the presence of MPS was confirmed by its peak at 3.73 min retention time. However, in the presence of Cu(II) ions, this peak did not appear; instead the typical peak of SPS^{2-} was found. The conversion efficiency was calculated to be above 99%. As a consequence, MPS is unlikely to be a major decomposition product of SPS in copper plating baths. This was indeed proved by spiking a plating bath sample with MPS; only an increase in the SPS peak was observed whereas no MPS peak could be detected.

4. Conclusions

A new and reliable chromatographic method for the determination of the brightener additive SPS in acidic copper plating baths was developed. Using tetra-*N*-methylammonium ion as ion-pairing agent in an eluent containing methanol–sulfuric acid–water, the anionic SPS^{2-} could be retained on a C_{18} column and separated from Cu(II) ion that is present in large quantities in these plating baths. No sample pre-treatment was necessary. The method proved sufficiently sensitive to measure SPS directly in plating bath samples. Moreover, some decomposition products that accumulate in the plating bath during its working lifetime, can also be monitored with this method, thus providing a fingerprint of by-product build-up. A surprising result of this study was that the suspected MPS decomposition product of SPS cannot exist in copper plating baths because it is converted quantitatively to SPS in the presence of Cu(II) ions. A full calibration study was performed for the analysis of SPS^{2-} in the relevant concentration range between 1.4×10^{-5} and 1.4×10^{-4} M. A new statistical approach was implemented in order to account for the "inexactness" of the SPS concentrations in the replicate calibration experiments. This method allowed us to calculate the weight factors needed for the WLS regression analysis. Application of the ion-pair chromatography analysis method to determine SPS in production plating bath samples revealed that the SPS levels in a commercial copper plating bath varied over a wide range although the SPS concentration in these samples was controlled independently by cyclic voltammetric stripping measurement, and was supposed to be at target level. This could have repercussions on the quality of the deposited copper films and the filling characteristics in narrow features. Consequently, reliance on cyclic voltammetric stripping as the only analysis technique for SPS, as is mostly practiced in the plating industry, could result in unreliable copper plating. Support from an analysis technique such as the one presented in this paper could help to elucidate possible problems with the cyclic voltammetric stripping measurement method and give more reliable SPS analysis data.

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