

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

### Modifications to the copper strip corrosion test for the measurement of sulfur-related corrosion

L. S. Ott<sup>a</sup>; T. J. Bruno<sup>a</sup>

<sup>a</sup> Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO, USA

**To cite this Article** Ott, L. S. and Bruno, T. J.(2007) 'Modifications to the copper strip corrosion test for the measurement of sulfur-related corrosion', *Journal of Sulfur Chemistry*, 28: 5, 493 – 504

**To link to this Article:** DOI: 10.1080/17415990701516432

**URL:** <http://dx.doi.org/10.1080/17415990701516432>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

RESEARCH ARTICLE

**Modifications to the copper strip corrosion test for the measurement of sulfur-related corrosion<sup>†</sup>**

L. S. OTT and T. J. BRUNO\*

Physical and Chemical Properties Division, National Institute of Standards and Technology,  
Boulder, CO, USA

(Received 27 March 2007; in final form 1 June 2007)

The copper strip corrosion test (CSCT) is used to measure the corrosivity of sulfur compounds in hydrocarbon fluids. The CSCT is performed by immersing a strip of cleaned, polished copper in a hydrocarbon fluid at a specified temperature for a predetermined time, then 'rating' the strip against a standard. In this work, instead of using the usual large, oblong strips designed to measure 30 mL fluid samples, we used small circular Cu 'coupons' as an alternative method for carrying out CSCTs on microscale samples of fluid. The motivations for reducing the scale include: applicability to small samples, ability to archive the small and inexpensive coupons, reduced waste, and potential for automated analysis using autosampler vials as reaction vessels. Moreover, the symmetric circular geometry facilitates the analysis of the images with mathematical color spaces. Mixtures of *n*-decane:*n*-tetradecane with varying concentrations of H<sub>2</sub>S (from a distillation column) were used as a source of microscale samples of corrosive fluid to demonstrate the viability of the smaller scale CSCT. Additional experimental details concerning the lighting conditions and digital photography of the coupons, measurement of corrosion using color space, and quantification of the sulfur content of the distillate are also described.

*Keywords:* Color space; Copper strip corrosion test; Sulfur impurities

## 1. Introduction

The corrosivity of certain sulfur species in fluid samples is determined using ASTM Standard Test Method D 1838 or D 130 (for liquefied petroleum gas and less volatile petroleum products, respectively), the copper strip corrosion test (CSCT) [1, 2]. In these tests, a strip of cleaned, polished copper is placed in a vessel that has been rinsed with water and then filled with an appropriate quantity of fluid. The filled vessel is then maintained at a predetermined temperature, ranging from 38 °C (100 °F) to 100 °C (212 °F), for 1–3 h (the temperature and time being determined by the characteristics of the fluid under study). Then, the strip is removed from the fluid and immediately rated. Rating a copper strip is done by comparison with lithographed standard strips provided by ASTM International. While it is not possible to

\*Corresponding author. Tel.: +1-303-497-5158; Fax: +1-303-497-5927; Email: bruno@boulder.nist.gov

<sup>†</sup>Contribution of the US Government; not subject to copyright in the USA.

reproduce the lithograph in this paper, we can describe it in general terms. The lithographs are divided into five classifications. First, a pristine, freshly polished strip is displayed on the ASTM lithograph; this pristine strip does not have a rating beyond 'freshly polished'. Next, four levels of progressive sulfur-related corrosion are presented: level 1 (with 1a and 1b, slight tarnish), level 2 (with 2a–2e, moderate tarnish), level 3 (with 3a and 3b, dark tarnish), and level 4 (with 4a–4c, severe corrosion). Strips 2c and 3b are both designated by the ASTM as 'multicolored', while the remaining ten standard strips have only one color descriptor.

Although the CSCT method is a well established standard, it is both qualitative and subjective [3]. Some disadvantages of the CSCT include: (a) all persons see color differently, which can result in different ratings of the same strip by different operators; (b) the ratings can be lighting dependent; (c) the lithograph has a nonlinear response progression (for example, 2d is vastly different from 2c, 2e is similar to 1a, and 3a is only slightly more tarnished than 1b); (d) the strips must be rated immediately after being removed from the fluid, which is sometimes difficult if the test is being performed in the field; (e) a freshly prepared strip never looks like that shown on the lithograph; (f) some of the color descriptors used on the lithograph, such as claret, are regionally uncommon and can be confusing; (g) the results of the test are very dependent on strip preparation; (h) failures can be caused by traces of some sulfur impurities, and large amounts of others. Furthermore, the proper procedure for the CSCT is not always followed (including residence time, temperature, sampling, and failing to use the lithograph). As a result of these factors, it has been noted that it is '...a rare occurrence to obtain a strip in routine work exactly matching any of these standards...' [4]. Clearly, a more quantitative and objective interpretation of the results of a CSCT is desirable.

In earlier work, we sought to make the interpretation of the copper strip corrosion test more quantitative and objective by analysing strips with mathematical color spaces [5]. A color space is a mathematical description of a range of colors, usually in three dimensions. Since color spaces use a well-defined numerical reference frames, they allow reproducible representations that are not device-dependent (for one example, using either a scanner or a camera to capture a image produces identical results in color space). One can mathematically pinpoint, and thus describe, a color in a given color space. Pinpointing a color in a color space is analogous to locating a position on a map with coordinates [6].

Three of the most common color spaces are RGB, HSB, and  $L^*a^*b^*$ . RGB color space uses red, green, and blue axes; HSB color space uses hue, saturation, and brightness axes; and  $L^*a^*b^*$  color space uses lightness ( $L^*$ ), the position on a continuum between red and green ( $a^*$ ), and the position on a continuum between yellow and blue ( $b^*$ ) for its axes. Of the common color spaces,  $L^*a^*b^*$  color space is the most complete color model for describing all the colors visible to the naked eye – i.e.,  $L^*a^*b^*$  color space covers the entire gamut of color. Additionally,  $L^*a^*b^*$  color space is perceptually linear; RGB and HSB are not.

Due to the advantages of  $L^*a^*b^*$  color space described briefly above, we used the  $L^*$  axis as a quantitative measure of the corrosion of copper strips used for CSCTs as part of earlier work to improve the copper strip corrosion test [5]. We found in that work that the lightness ( $L^*$ ) of a copper coupon was well correlated with the observed copper corrosion, with slightly tarnished strips having a high value for  $L^*$  and severely corroded strips having a low value for  $L^*$ . Before applying color space analysis to the copper strips, the  $L^*$  values of each strip on the ASTM-provided lithograph were measured. Then, the  $L^*$  values of copper strips used for CSCTs were measured and compared with the  $L^*$  values measured for the lithograph. In this manner, the CSCT results were more quantitatively and objectively interpreted, avoiding many of the disadvantages of the CSCT listed earlier. Indeed, one can perform this same kind of color space analysis to the lithograph itself. Plots of the  $L^*$ ,  $a^*$  and  $b^*$  readings for each of the strips on the lithograph are shown in figure 1 [5]. This figure has a dual purpose. First, it points out many of the idiosyncrasies of the lithograph, such as those discussed earlier. The

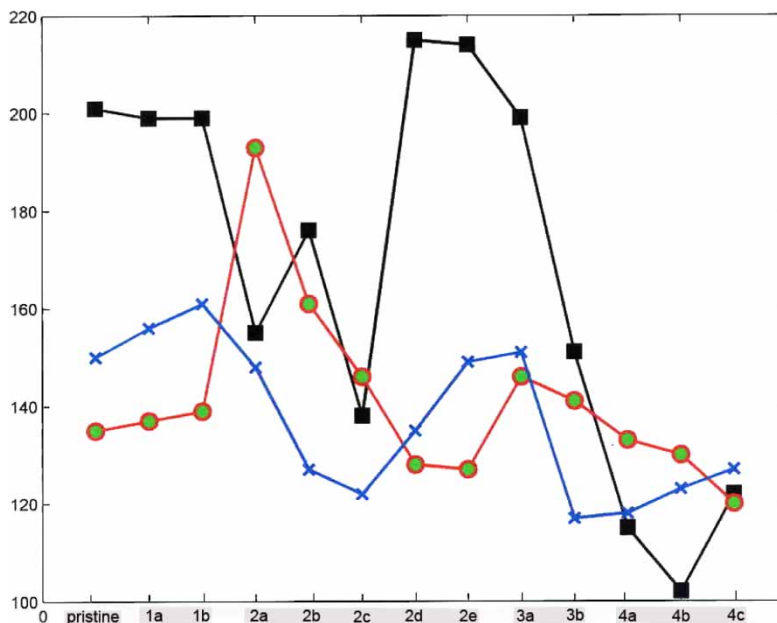


Figure 1. Measurement of the  $L^*$  (filled square markers),  $a^*$  (circle markers) and  $b^*$  (cross markers) values for the ASTM-provided lithograph standard.

$L^*$  values, for example, clearly show the similarity between the 1b and the 2e and 3a ratings. The strips not only look very similar, but by an objective measure ( $L^*$ ), they indeed are very similar. Second, the graph is valuable as a guide in the interpretation of color space analyses of actual sample coupons. Measuring the  $L^*$  values of the lithograph in  $L^*a^*b^*$  color space (which, recall, is a device-independent color space) yields values that are considered as fixed points with essentially no describable uncertainty.

In this work, we report a modification to the CSCT that has the potential to extend the applicability of the test. Instead of the typical large oblong copper coupons (as specified in the standards), we demonstrate here the workability and advantages of very small circular copper coupons. The small size of the coupons we use makes the test suitable for use with very small samples. The CSCT (as detailed in the ASTM D 130 standard) was designed for 30 mL fluid samples [2]. Consequently, the copper strips used for those tests are relatively large, 12.5 mm wide, 1.5 to 3.0 mm thick, and 75 mm long. These large strips are not practical for samples where only microscale quantities of the fluid are available. Moreover, the oblong copper strips are not ideal for the application of mathematical color space analysis, while the circular geometry of the smaller coupons actually facilitates such analysis. There are other advantages to the use of the smaller strips. There is far less waste generated per test when the small coupons are used, which is an important environmental and legal consideration. The ability to archive and maintain the test coupons as part of a permanent record (for quality control and legal purposes) is another important advantage; the small coupons are very economical and easy to preserve and store. There is no sacrifice of information; all the color ranges and variations discerned on the larger strips are as visible on the smaller coupons. Finally, the tests can be performed in analytical automatic sampler vials, which facilitates coupling the CSCT with other analytical procedures that can be performed on the same sample.

As a test of this modified approach to the CSCT, we applied the method to distillate cuts of a hydrocarbon mixture (50:50 mol percent *n*-decane:*n*-tetradecane) that was spiked with hydrogen sulfide. The distillate cuts emerging from a condenser were sampled (as a function

of distillate volume fraction, as in the measurement of a distillation curve [7]) and, therefore, provide a changing concentration of hydrogen sulfide as the distillation progresses. This simply serves as a way to generate a series of samples that will show a predictable range of sulfur concentrations. Each emergent distillate sample was tested by the CSCT. Additionally, and to complement the CSCT results, each distillate sample was analysed for H<sub>2</sub>S concentration by gas chromatography with sulfur chemiluminescence detection (GC-SCD).

## 2. Experimental section

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier, and was analysed by gas chromatography (30 m capillary column of 5% phenyl-95%-dimethyl polysiloxane having a thickness of 1 μm, temperature program from 50 to 170 °C, 5 °C per minute) using flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be approximately 99.95%, and the fluid was used without further purification. The acetone and toluene used to scrub and store the copper coupons were obtained from a commercial supplier with stated purities greater than 99.5% and were used as received. The two fluids were stored at 7 °C prior to use.

The *n*-decane (C<sub>10</sub>) and *n*-tetradecane (C<sub>14</sub>) used in this work were obtained from a commercial source. The fluids had a purity specification of 99.9% (mass/mass), which was verified by gas chromatography. The fluids were, therefore, used without further purification. Stock solutions of 50:50 (mol/mol) C<sub>10</sub>:C<sub>14</sub> were prepared volumetrically and stored in sealed 500 mL plastic bottles at 7 °C. The stock solutions were used within one day of preparation.

Hydrogen sulfide was obtained from a commercial supplier with a purity specification of greater than 99.5% (mass/mass). The stock solutions of C<sub>10</sub>:C<sub>14</sub> were bubbled with the H<sub>2</sub>S for predetermined amounts of time to dissolve variable quantities of this corrosive sulfur compound. Care must be exercised with H<sub>2</sub>S, which is flammable, has broad explosive limits in air, and may cause asphyxiation leading to death when inhaled. The dimethyl sulfoxide that was used for calibration of the sulfur chemiluminescence detector was obtained from a commercial source with a stated purity of 99.9% (mass/mass). The bottle was stored tightly sealed to minimize the adsorption of water, which is sufficient to exclude most moisture due to the low humidity in Boulder, CO, USA. The purity had been verified in earlier work by gas chromatography and sulfur chemiluminescence detection, and the fluid was used without further purification.

The stock solutions of C<sub>10</sub>:C<sub>14</sub> with dissolved H<sub>2</sub>S were distilled in 200 mL portions using a distillation curve apparatus that has been modified to allow on-the-fly sampling of the distillate via a modified receiver adapter [8, 9]. Eleven distillate aliquots of approximately 10 μL each (labeled as fractions A–K, and corresponding to distillate volume fractions from 0.025% to 80%) were removed during the course of the distillation and used for CSCT fluid samples.

The Cu coupons used for the CSCTs were punched from an electrolytic tough pitch copper sheet, and were approximately 5 mm in diameter and 0.75 mm in thickness; these coupons fit conveniently in the bottom of the wide-mouth GC autosampler vials. Each coupon had a slightly concave side and a flat side, resulting from punching the coupon out of the metal sheet. The coupons were polished on their flat sides with a rotary wheel coated with an abrasive polishing compound, similar to the ASTM recommendation of a ‘motor-driven machine using appropriate grades of dry paper or cloth.’ [2] The coupons were polished for 30–60 s, until the oxide layer atop each coupon was removed and the surface appeared uniformly smooth. The standards recommend a ‘final polishing’ step with a larger mesh grit paper to roughen the surface of the copper; however, this step is impractical using the coupons, given their small

size. Moreover, the surfaces of the coupons are adequately rough because their surfaces have been polished only with a fine grit polishing compound, leaving some inherent roughness of the copper metal surface. Since only one side of the coupons was polished, the small coupons have 220–240 times less surface area than the standard oblong strips (the precise ratio being dependent on the thickness of the strip). The ASTM guidelines also recommend cleaning all metal dust and shavings from the copper surface with absorbent cotton [2]. Consequently, the coupons were scrubbed with cotton swabs soaked in 50:50 acetone:toluene to remove any residual polishing compound. The polished coupons were stored in 50:50 acetone:toluene until use.

The autosampler vials used for the CSCTs were rinsed with approximately 1.5 mL deionized water. This left a small amount of water in the vial, as specified in the standards. Then, a Cu coupon was removed from the acetone:toluene storage solution, rinsed in acetone, dried to remove any excess solvent, and placed at the bottom of the vial. The vial was filled with ~0.7 mL *n*-hexane and sealed with a crimp-cap with a silicone septum (see figure 2 for a drawing of a ‘prepared’ vial). Then, ~10  $\mu$ L of distillate was injected through the silicone septum.

After injection of the distillate into the vial, each vial was agitated on a vortex plate for 5 s to ensure sufficient mixing. Then, each vial was further capped with a rubber cover over the crimp-cap to minimize H<sub>2</sub>S permeation and loss through the pierced septum. The rubber caps were fabricated by cutting the bottom off 1 mL rubber bulbs. The vial was then placed in a stirred water bath maintained at 38.5 °C (100 °F) for 1 h, as specified in the ASTM standards. After 1 h, the vial was removed from the water bath, its rubber cap removed, the crimp-cap uncrimped, and the solution decanted. The Cu coupons were then dried and rated with the ASTM D130/IP 154 lithograph.

Since we required a faithful digital reproduction of the Cu coupons for the  $L^*a^*b^*$  color space analysis, we performed a series of survey tests to determine how best to reproduce the visual appearance and features of the coupons. These tests included making photographic images of the coupons with several scanners and digital cameras. We found that the digital camera performed best, and that the flat side of the coupon consistently provided the best image in terms of reproducing what is seen visually.

For photographing the Cu coupons, gray cards were used to provide a background with a neutral reflectance of 18% (based on the standard reflectance with which light meters are calibrated) [10]. The 11 Cu coupons from each distillation were mounted with craft glue onto a gray card in a circular pattern. The coupons were mounted in a circle to promote uniform lighting conditions over the coupons. Next, the gray card was centered on a rotary table typical of the type used in machine shop operations. A semi-opaque white light diffuser (made from a large polyethylene carboy) was used to cover the gray card on the rotary table. The diffuser was used to provide indirect lighting without reflection off the coupons’ surfaces. The digital camera was mounted on a tripod to suspend the camera directly atop the opening to the carboy. The mouth of the carboy was encircled with black felt to protect the camera

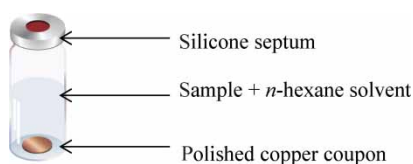


Figure 2. A schematic diagram of an autosampler vial prepared with *n*-hexane solvent and a polished Cu coupon for a small scale CSCT.

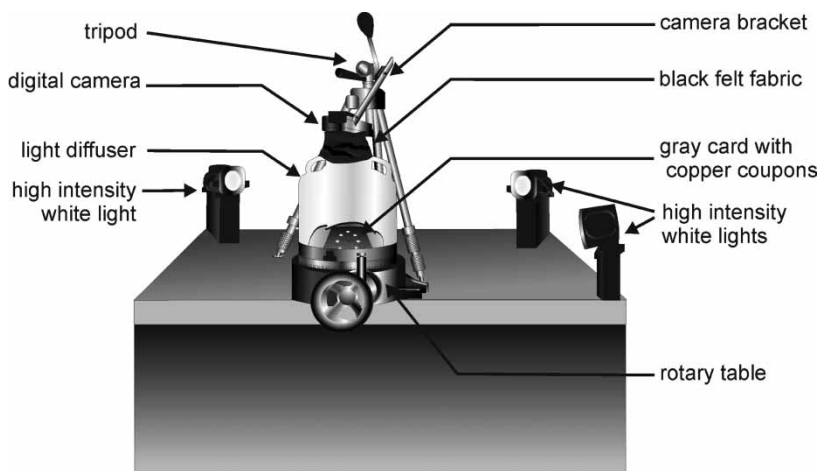


Figure 3. A schematic diagram of the set-up used for digital imaging of the Cu coupons. Note that the gray card with the copper coupons mounted on it is underneath the light diffuser.

from being saturated with stray light. The room lights were extinguished, and the diffuser was illuminated with three high intensity white photography lights (see figure 3).

The camera collected image data in raw format, which was subsequently converted to tif format. Next, the tif images were imported into a commercially available digital imaging software package. The imaging software was used to capture the largest circular area of each coupon without including any coupon edges. The same size circular 'lasso' was used for each coupon in a series. The captured circular areas were viewed and analysed in  $L^*a^*b^*$  color space.

To minimize uncertainty and avoid aberrant  $L^*$  measurements due to shadowing on the coupons, five images of each gray card (containing the coupons) were captured, rotating the circle of coupons about the center after each image was captured. Thus, the first digital image was collected with the rotary table set at zero degrees, and then three additional images were obtained at 90 degree increments on the rotary table. Finally, a fifth image that repeated the first image (i.e., with the rotating table again set to zero degrees) was collected. The  $L^*$  values that are reported herein are a numerical average of the five individual  $L^*$  measurements collected following the procedure outlined above. The standard deviation and standard uncertainty of the five  $L^*$  values were calculated for each coupon [11]. The expanded ( $k = 2$ ) uncertainty was between 5% and 6% of the mean value in each case.

As alluded to earlier, on a very small number of images, a shadow was cast on a coupon by: (1) a slightly bent coupon, (2) an uneven mounting of the coupon on the gray card, or (3) non-uniform lighting conditions. The presence of a shadow (not to be mistaken for corrosion) was detected by comparing the apparently shadowed coupon over the five digital images of the gray card; if the darkened area of the coupon appeared on different sides of the coupon or was not present in one or more of the images, it was determined to be a shadow. In the case of a shadow, the  $L^*$  value was measured by using an area of the coupon that did not include the shadowed (and thus artificially low  $L^*$  valued) portion of the coupon. This area is necessarily smaller than the area described above, which was intended to capture the largest possible portion of the coupon. We found that this procedure did not markedly change the uncertainty.

Additionally, a few coupons showed small, distinct, stained spots. The presence of the stains on copper strips during the CSCT is well known and is discussed in the ASTM standards. In the case of stains, the  $L^*$  value of the coupon was determined by excluding the stained portion(s)

in a manner similar to that described above for the shadowed coupons. This is consistent with the usual interpretation of CSCT strips as specified in the ASTM standards.

The ASTM standards also outline a series of procedures used to distinguish between two CSCT ratings when a given strip cannot be easily read as one of the two ratings (as one example, a solvent immersion test is used to determine whether a strip should be read as 2a or 3a [2]). These procedures are not addressed in the present work since our aim is to use the  $L^*$  parameter to rate the copper coupons.

In addition to carrying out a CSCT on each distillate fraction and measuring the  $L^*$  values, the  $H_2S$  content of each distillate fraction dissolved in  $n$ -hexane was analysed on a commercially available gas chromatograph, equipped with a sulfur chemiluminescence detector [12]. A background correction was performed using  $n$ -hexane; the non-zero response of the sulfur chemiluminescence detector to  $n$ -hexane was subtracted from each of the sample values to obtain the corrected sulfur signal. The sulfur concentration in each vial was calculated using a calibration curve prepared with solutions of dimethyl sulfoxide. A sample of each prepared stock solution of  $C_{10}:C_{14}$  with dissolved  $H_2S$  was analysed by GC-SCD to determine the initial concentration of  $H_2S$  in each solution.

### 3. Results and discussion

To demonstrate the modified CSCT, we present representative results from four separate measurements of the distillation curves of the  $n$ -decane +  $n$ -tetradecane mixtures spiked with  $H_2S$ . For each, we present the results of the CSCT, the  $L^*a^*b^*$  color space analysis, and the result from the sulfur chemiluminescence detector. The results from the four distillations are presented in table 1 (which reports the CSCT ratings,  $H_2S$  concentration, and  $L^*$  measurements) and figures 4–7 (which show the coupon images). The  $L^*$  values that are presented are the averages of five separate measurements, as described earlier.

Figure 4 shows the coupons from a distillation with an initial  $H_2S$  concentration of 3.6 mM. Dark tarnishing of the coupons occurred only for the first three volume fractions sampled, corresponding to coupons A (0.025%), B (10%), and C (20%). While coupons A and B look different in the figure, they are both rated as 3b. This is because both coupons A and B match separate regions of the (non-uniform) strip 3b on the lithograph standard. Magnification of the digital image of coupon A revealed that nearly 50% of the coupon appeared green and there was

Table 1. CSCT ratings and  $L^*$  values for each coupon shown in figures 4–7, as well as GC-SCD data measuring the hydrogen sulfide concentration (in mM) of the distillate dissolved in  $n$ -hexane solvent corresponding to the coupons shown in figures 4 and 5.

Sample	Vol. fraction	Figure 4			Figure 5			Figure 6		Figure 7	
		CSCT	( $[H_2S]$ )	$L^*$	CSCT	( $[H_2S]$ )	$L^*$	CSCT	$L^*$	CSCT	$L^*$
A	0.025	3b	0.34	170	4a	6.40	78	3b	120	3b	87
B	10	3b	0.28	96	3b	3.00	105	2e	186	3b	127
C	20	3a	0.18	170	3b	1.44	158	3b	139	2d/2e	191
D	30	1a	–	198	3a/3b	0.73	170	3b	107	3a	180
E	35	1a	–	200	3a/3b	0.54	142	3a	145	2c	158
F	40	1a	–	199	2b	0.37	109	1a/1b	179	3a	163
G	45	1a	–	199	2b	0.38	134	1a/1b	193	1a/1b	189
H	50	1a	–	202	2e	0.16	184	1a/1b	196	1a/1b	198
I	60	1a	–	201	1a/1b	–	199	1a/1b	199	1a/1b	203
J	70	1a	–	201	1a/1b	–	201	1a/1b	201	1a/1b	200
K	80	1a	–	201	1a/1b	–	193	1a/1b	195	1a/1b	194



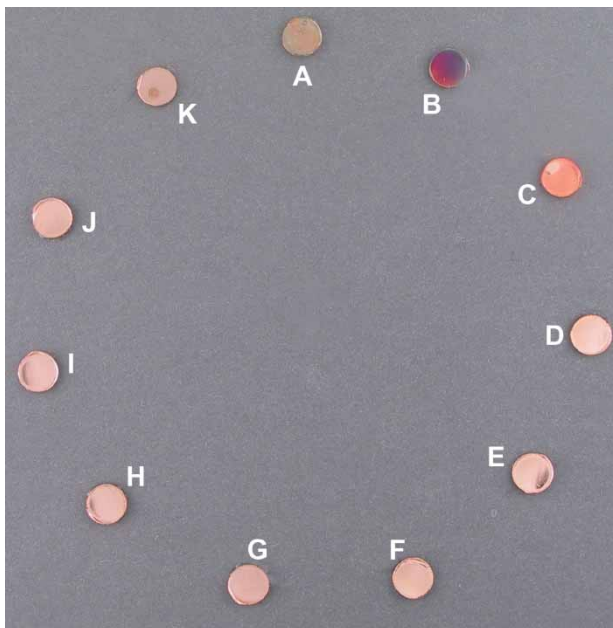


Figure 4. Cu coupons from a distillation with an initial  $\text{H}_2\text{S}$  concentration of 3.6 mM.

also significant tarnishing. The observed 'peacock' green color and significant tarnishing are characteristic of a 3b rating. This illustrates the value of capturing digital images of the coupons and examining their magnified images as part of the CSCT analysis, as we demonstrated in earlier work [3].

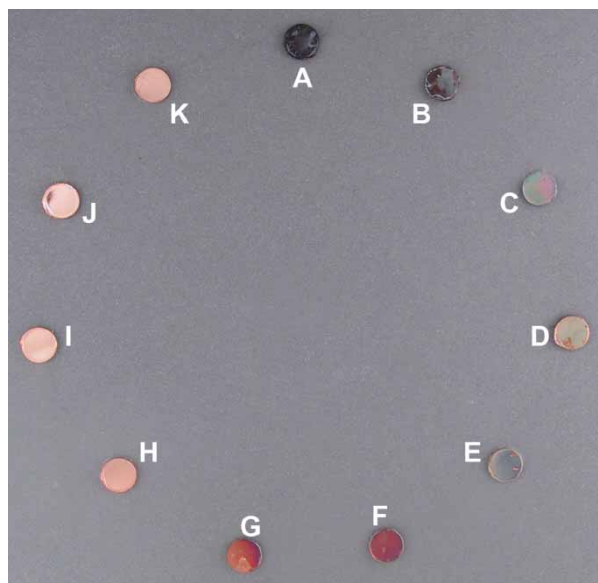


Figure 5. Cu coupons from a distillation with an initial  $\text{H}_2\text{S}$  concentration of 57 mM.

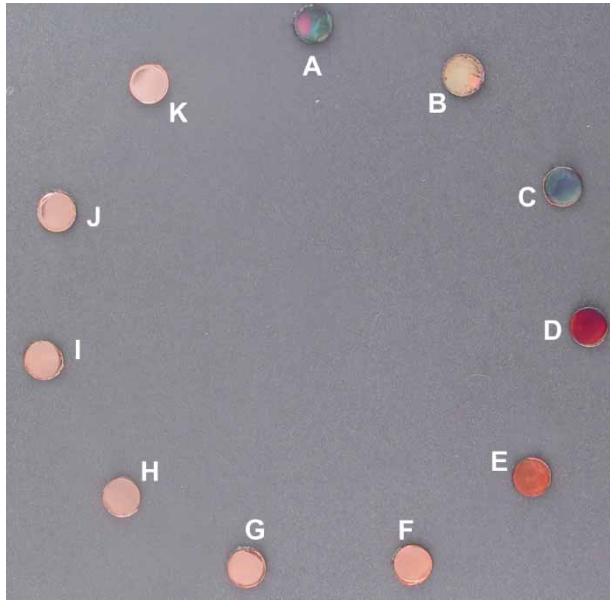


Figure 6. Cu coupons from a distillation with an initial  $\text{H}_2\text{S}$  concentration of 30 mM.

The remaining coupons in figure 4, labeled D–K, were all rated 1a. A rating of 1a corresponds to very slightly tarnished coupons; indeed, coupons D–K in figure 4 are indistinguishable from freshly polished coupons. Therefore, distillate volume fractions that emerged at the 30% volume fraction or higher were not corrosive as determined by the CSCT.

To complement the CSCT ratings, gas chromatography with sulfur chemiluminescence detection (GC-SCD) was employed to determine the  $\text{H}_2\text{S}$  content in each autosampler vial.

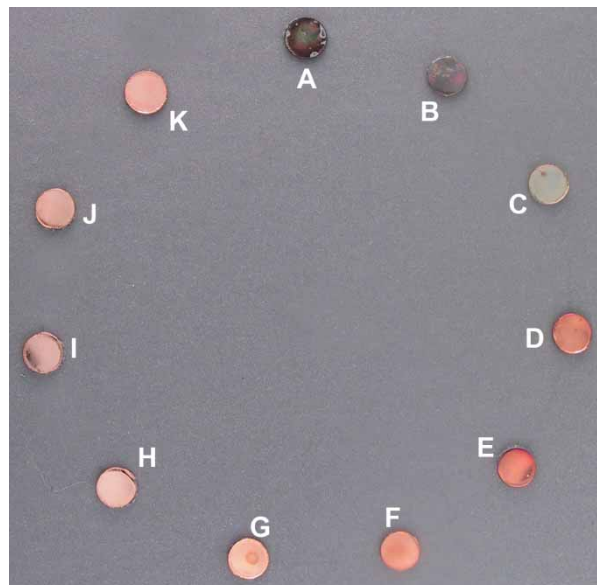


Figure 7. Cu coupons from a distillation with an initial  $\text{H}_2\text{S}$  concentration of 22 mM.

GC-SCD is a rapid method that responds in an equimolar fashion to the total sulfur content [13, 14]. For the coupons shown in figure 4, table 1 reports the sulfur content for the first three distillate volume fractions – the sulfur content for the remaining fractions is so low that it cannot be quantified above the background signal of *n*-hexane. This result shows that only the tarnished coupons had measurable sulfur content. The sulfur content for the diluted distillate ranged from 0.34 to 0.18 mM for the first three distillate cuts (points A–C). Therefore, a quantifiable correlation between the sulfur concentration of the solution and the CSCT rating exists for the specific case of corrosion caused by dissolved H<sub>2</sub>S.

As a second example of the modified CSCT, figure 5 shows the coupons from a distillation with an initial H<sub>2</sub>S concentration of 57 mM. In this experiment, the first eight coupons show tarnishing, a greater number than in the preceding experiment, which began with a lower initial concentration of H<sub>2</sub>S. Coupon A in figure 5 is rated 4a, indicative of severe corrosion, while coupons B–E display the variations on color characteristic of the 3b lithograph standard strip.

Consistent with the results shown in table 1 for figure 4, only the coupons in figure 5 that showed tarnishing by the CSCT had sulfur concentrations that were measurable by GC-SCD. Moreover, higher concentrations of sulfur correlate well with more extensive corrosion of the Cu coupons as measured by the CSCT. In agreement with the results shown for figure 4, the coupons in figure 5 that rate above 1a or 1b on the CSCT have a total solution concentration greater than or equal to  $\sim 0.15$  mM H<sub>2</sub>S. As we found in earlier work using the larger Cu strips [3], the  $L^*$  values correlate with the corrosion of the coupons. Severely corroded coupons have low  $L^*$  values, and slightly tarnished coupons have high  $L^*$  values.

Figures 6 and 7 show the coupons used for CSCTs for two separate distillations that had initial H<sub>2</sub>S concentrations of 30 and 22 mM, respectively. These 22 coupons show further that the small coupons are capable of portraying the variegations in color that are typical of some of the lithographed standards (for example, standards 3b and 2c). Additionally, coupon G in figure 7 illustrates the staining phenomena discussed in the experimental section, while coupon I is a good example of a coupon that has one edge shadowed.

For the coupons showing dark tarnish that were rated 3b, there was a relatively large difference in the measured  $L^*$  values. The difference in measured  $L^*$  values for coupons rated 3b is due to the color disparities in the coupons (for example, compare coupons A and B in figure 7). The color disparities in the coupons are to be expected, given the wide color disparity on the lithograph standard strip 3b. The wide range in  $L^*$  values for coupons rated 3b, encompassing values from 87 to 170 in the present case, might be considered characteristic of the 3b rating.

Measuring the  $L^*$  values of the coupons opens the door for quantitatively rating their corrosion. To quantitatively rate the coupons, the  $L^*$  values for each CSCT rating must be reproducible between experiments. This reproducibility weighs heavily on the uniformity of the lighting conditions during digital imaging of the coupons. To assess the reproducibility of the lighting conditions, comparison of samples that are rated 1a or 1b is one good approach, since these two standard strips have uniform color and lightness. Table 1 shows that the  $L^*$  values of the slightly tarnished coupons are consistent within the uncertainty of the measurements for the coupons rated 1a, 1b, or 1a/1b in the 44 coupons shown in figures 4–7. Since the photographs shown in figures 4–7 were taken over the course of several weeks, this demonstrates that the lighting conditions are reproducible between experiments.

Furthermore, the uniformity of the lighting conditions over the 11 circularly mounted coupons on each gray card was investigated by examining the measured  $L^*$  values for each coupon over the five digital images produced by rotating the rotary table in 90° increments. Overall, the measured  $L^*$  value for a coupon in a single position was typically within five units of the mean  $L^*$  value for the same coupon averaged over the five positions on the rotary

table. For one example, the measured  $L^*$  value for each image of coupon K in figure 4 did not deviate by more than 3% from the mean  $L^*$  value for the coupon.

Finally, the  $L^*$  values of all of the coupons shown in figures 4–7 were compared with values previously measured for the standard strips. These values for the majority of the coupons correlate well with the values measured for the lithograph standards – table 1 and figure 1. The measured  $L^*$  values for the coupons that rated 2c or 3b do not in every case correlate with the value measured for the lithograph. As briefly discussed earlier, this is due to wide color and lightness variegations on the lithograph standards for these two strips. These wide variegations mean that the  $L^*$  value measured for the lithograph is an *average* over all of the colors and lightnesses present on the standard strip, while the  $L^*$  value measured for a coupon may correspond only to the lightness in one part of the lithograph.

Overall, except for the coupons that rated 2c or 3b, the rest of the coupons'  $L^*$  values correlated perfectly with the lithograph  $L^*$  values, with the criterion being of a go-no-go variety. The fact that the values measured for the small, circular coupons correlate with the values measured for the larger, rectangular strips indicates that the smaller size of the coupon compared with the larger strip does not result in a significant difference in the measured  $L^*$  value. Consequently, the  $L^*$  values of the coupons can be used to quantitatively rate the coupons by the CSCT.

#### 4. Conclusions

Herein, we have demonstrated that the CSCT can be scaled down for use with microscale quantities of corrosive fluid. The small Cu coupons are capable of measuring corrosion induced by added  $H_2S$ , also showing the variegations in color that are characteristic of some of the standard strips on the ASTM lithograph. Carrying out the CSCT in autosampler vials allows the use of automated chemical analysis, such as GC-SCD, to complement the results of the CSCT. Additionally, the small coupons minimize waste and allow for inexpensive archiving. Digital images of the symmetric coupons can be used to quantitatively measure the  $L^*$ , and thus the corrosion, of the coupons. Mounting the coupons in a circular pattern on gray cards yielded uniform lighting conditions and consistent  $L^*$  values.

#### Acknowledgements

This work was carried out while LSO held a National Academy of Sciences/National Research Council Postdoctoral Associateship Award at NIST.

#### References

- [1] American Society for Testing and Materials. Standard test method for detection of copper corrosion by liquefied petroleum (LP) gases, ASTM Standard D 1838–91, West Conshohocken, PA (1991 (Reapproved 2001)).
- [2] American Society for Testing and Methods. Standard test method for detection of copper corrosion from petroleum products by the copper strip tarnish test; ASTM Standard D 130, West Conshocken, PA (2004).
- [3] W.C. Andersen, A.I. Abdulagatov, T.J. Bruno. *Energy & Fuels*, **17**, 120 (2003).
- [4] F.W.H. Mathews, D.F. Parsons. The copper-strip test—a study of current methods of interpretation and an examination of proposed new procedures. Proceedings of the Mid-Year Meeting, American Petroleum Institute (1950).
- [5] W.C. Andersen, G.C. Straty, T.J. Bruno. Improving the copper strip corrosion test. Proceedings of the GTI Natural Gas Technologies Conference and Exhibition, Phoenix, AZ (2004).
- [6] C. Poynton. Available online at: [www.poynton.com/PDFs/ColorFAQ.pdf](http://www.poynton.com/PDFs/ColorFAQ.pdf) (accessed 15 December 2006).
- [7] W.L. Leffler. In *Petroleum Refining in Nontechnical Language*, PennWell, Tulsa, Oklahoma (2000).
- [8] T.J. Bruno. *Separation Sci. Technol.* **41**, 309 (2006).
- [9] B.L. Smith, T.J. Bruno. *Int. J. Thermophys.*, **27**, 1419 (2006).

- [10] Available online at: <http://www.acecam.com/magazine/gray-card.html> (accessed 9 January 2007).
- [11] B.N. Taylor, C.E. Kayatt, *Guidelines for evaluating and expressing the uncertainty of NIST measurement results*; NIST Technical Note 1297, National Institute of Standards and Technology, Gaithersburg, MD (1994).
- [12] T.B. Ryerson, A.J. Dunham, R.M. Barkley, R.E. Sievers. *Anal. Chem.*, **66**, 2841 (1994).
- [13] W.C. Andersen, T.J. Bruno. *Ind. Eng. Chem., Res.*, **42**, 963 (2003).
- [14] W.C. Andersen, T.J. Bruno. *Ind. Eng. Chem. Res.*, **42**, 971 (2003).