Donnan equilibrium/graphite furnace atomic absorption estimates of soil extract complexation capacities
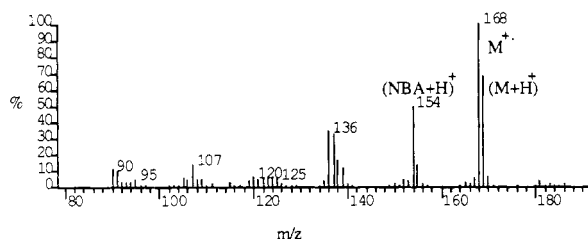
2 **AUTHORS**, INCLUDING:

Alanah Fitch
Loyola University Chicago

58 PUBLICATIONS **984** CITATIONS

Figure 3. Positive ion FAB spectrum of NBA on stage "A" and 1,3,5-trimethoxybenzene on stage "B" of the dual stage FAB target.

to occur. The converse is not true.

Figure 3 shows the positive ion FAB spectrum of NBA placed on sector "A" in the presence of TMB on sector "B". Both TMB$^{+\bullet}$ and (TMB + H)$^+$ are observed, a spectrum very similar to that of Figure 2, where the analyte and matrix were a solution. This provides conclusive evidence for the gas-phase mechanism, since the (M + H)$^+$ ion does not arise in the absence of the matrix. Yet the two materials were on different probe segments. If one or the other sample was removed from the probe tip after several scans, the remaining sample did not show any cross contamination from one liquid sample to the other.

If we used a glycerol matrix for TMB rather than NBA or NPOE, then instead of the analyte dominating the spectra, the analyte peaks, M$^{+\bullet}$ and (M + H)$^+$, are less than 10% the intensity of the glycerol peak at m/z = 93. It is not clear why glycerol is such a poor matrix for TMB, but this is characteristic of many FAB systems.

Ions corresponding to M$^{+\bullet}$ and (M + H)$^+$ are absent in the positive ion FAB spectra of BHD either with or without matrix. The molecule lacks ready sites for protonation, so the lack of (M + H)$^+$ is not surprising. The lack of a molecular ion may be attributable to an ionization potential higher than 10 eV. We have found that ions corresponding to M$^{+\bullet}$ are not observed in FAB for compounds having ionization potentials higher than 9 eV (8). The relative intensity of ions corresponding to the (BHD – H)$^+$ ion with respect to m/z 97 (which probably corresponds to C$_7$H$_{13}^+$) varies from 6% in NPOE, 18% in glycerol, and 23% in NBA to 28% for the pure material, vs ~40% for the reported EFAB (6). By use of our divided probe with NBA on side "A" and BHD on "B", the relative intensity of (M – H)$^+$ to m/z 97 was 8.6%, perhaps due to the relatively low volatility of BHD. Certainly, a significant portion of the m/z 303 arises from gas-phase ionization.

The negative ion FAB mass spectra of nitroaromatic compounds obtained by using a glycerol matrix are summarized in the Table I. All species studied showed molecular ions corresponding to M$^{-\bullet}$ and most of the peaks are fairly intense, e.g. 37% and 94%, respectively, for 1,3-dinitrobenzene and 4-nitrophenylacetonitrile, compared to the glycerol dimer which dominates the spectrum at m/z 183. Analyte/glycerol

interaction also occurs as we see ions corresponding to (M + nGly)$^{-\bullet}$, n = 1–4. Nitroaromatic compounds also produce abundant M$^{-\bullet}$ ions from NPOE and NBA matrices (8, 9). NBA is also a good matrix for compounds such as vitamin K$_1$ for which the negative ion EFAB has been reported (16). We find this spectrum is dominated by ions corresponding to M$^{-\bullet}$. These two matrices, NBA and NPOE, are commonly used in the study of nonpolar organic, organometallic, and coordination compounds (8, 9, 11). The above data show that careful selection of matrix results in one obtaining reasonable mass spectra for nonpolar nitroaromatic compounds.

CONCLUSIONS

We have demonstrated that excellent FAB mass spectra under normal FAB conditions can be obtained for nonpolar compounds such as those pioneered by Bartmess and Phillips in their EFAB work (6, 16). For this purpose the NBA matrix pioneered by Meili and Seibl is preferred (10). We also show that glycerol can be used as a matrix for nitroaromatic compounds as long as a cosolvent is used to aid dissolution.

LITERATURE CITED

(1) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, 325.
(2) Fenselau, C.; Vu, V. T.; Cotter, R. J.; Hansen, G.; Heller, D.; Chen, T.; Colvin, O. M. *Spectroscopy: Int. J.* **1982**, *1*, 32.
(3) Fenselau, C. *J. J. Nat. Prod.* **1984**, *47*, 215.
(4) Miller, J. M. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 1.
(5) Bruce, M. I.; Liddell, M. J. *Appl. Organomet. Chem.* **1987**, *1*, 191.
(6) Bartmess, J. E.; Phillips, L. R. *Anal. Chem.* **1987**, *59*, 2014.
(7) Huang, G.-W.; Wu, G.-L.; Tang, H.-T. *Int. J. Mass Spectrom. Ion. Processes* **1986**, *70*, 145.
(8) Balasanmugam, K.; Miller, J. M.; Smith, R. W. *Org. Mass Spectrom.* **1988**, *23*, 685.
(9) Balasanmugam, K.; Miller, J. M. *Org. Mass Spectrom.* **1988**, *23*, 267.
(10) Meili, J.; Seibl, J. *Org. Mass Spectrom.* **1984**, *19*, 581.
(11) Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. *Inorg. Chem.* **1987**, *26*, 560.
(12) Miller, J. M.; Fulcher, A. *Can. J. Chem.* **1985**, *24*, 397.
(13) Balasanmugam, K.; Hartman, J. S.; Miller, J. M.; Yuan, Z. *Can. J. Chem.*, in press.
(14) Miller, J. M.; Balasanmugam, K.; Fulcher, A. *Org. Mass Spectrom.*, in press.
(15) Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements 1971-1981*; National Bureau of Standards: Washington, DC.
(16) Bartmess, J. E.; Phillips, L. R. *Proc. 36th ASMS Conf. Mass Spectrom.* **1988**, 1198.

Jack M. Miller*
Kesagapillai Balasanmugam
Department of Chemistry
Brock University
St. Catharines, Ontario, Canada L2S 3A1

Donnan Equilibrium/Graphite Furnace Atomic Absorption Estimates of Soil Extract Complexation Capacities

Sir: Organic complexing materials are known to affect the speciation of metal ions in soil solutions which, in turn, influences the bioavailability of these minerals to plants and their transport through the soil (1–3). Determination of soil

solution complexing capacities has been made by solvent extraction and ion exchange methodologies (4–8). These measurements depend upon accurate knowledge of stability constants of known ligands and may involve changes in so-

lution composition due to the lability of natural complexing agents in the presence of the added ligands. As a consequence, the measured magnitude of the uncomplexed ion can deviate from the equilibrium solution values, thus imparting error to the measurement of the soil solution complexation capacity. As an alternative method, naturally occurring ligands may be titrated to determine the total complexing capacity (9). The uncomplexed (free) concentration of a strongly complexed ion, such as Cu^{2+}, may be analyzed by a variety of techniques. Common methods of following the Cu^{2+} concentration have been anodic stripping voltammetry (ASV) and ion selective electrode potentiometry (ISE). In ASV, the measured Cu^{2+} is often the sum of the uncomplexed metal and some fraction of the metal complex which dissociates in response to the measurement. Electrode fouling may also occur. In ISE, the lower limit of detection can be unacceptably high. A method that has a low limit of detection and that minimizes electrode fouling and ligand lability is desirable.

One promising approach is to separate the cationic species of interest from the substrate solution without perturbing the substrate solution equilibrium via Donnan equilibrium (DEq) across an ion exchange membrane (10–13). When acceptor solution is high in ionic strength relative to the substrate solution, enrichment of cations can occur. This technique, Donnan dialysis, has been extensively studied (14–18). When the acceptor solution and substrate ionic strengths are matched, the concentrations of the cations in the acceptor and substrate solutions are equal. Cation selectivity is the result of the variation in the rate at which Donnan equilibrium is achieved for cationic, neutral, and anionic species (18). Because the membrane is negatively charged, the flux of cations is more rapid than the flux of anions and equilibrium for these species is achieved more rapidly. For many high molecular weight neutral species the flux is slower than for the cation because membrane size exclusion can occur (18).

Following equilibration, the total metal concentration in the acceptor solution can be measured by any of a number of techniques which have a suitable limit of detection. In this paper we give preliminary results in coupling DEq with graphite furnace atomic absorption (GFAA) measurements of copper for the estimation of complexing capacities of extracts of sludge amended soils.

MATERIALS AND METHODS

Reagents. All reagents, analytical grade, were used without further purification. Stock solutions were prepared from the metals, diluted by weight with 0.01 M $Sr(NO_3)_2$ prepared in distilled deionized water, and stored in acid-rinsed linear polyethylene containers that had been checked for adsorption/desorption of cadmium and copper. Stock solutions were diluted with 0.01 M $Sr(NO_3)_2$ to make working curves as necessary.

Extractant. The extractant electrolyte concentration should be large enough to mask the actual concentration of electrolyte deriving from the sample. Since typical soil solutions contain 0.008 M in Ca^{2+} (19), a 0.01 M extractant was used. It was determined that $Ca(NO_3)_2$ resulted in interferences in the GFAA analysis of Cd^{2+} and, therefore, $Sr(NO_3)_2$ was chosen as an extractant. To investigate the effect of the extractant volume on the concentration of the water-soluble complexing material, two ratios, 1/2 and 1/25 grams of soil per grams of extractant, were used.

Soils. Plano silt loam (Typic Argiudoll) soils from Arlington, WI, amended with Chicago Metropolitan sludge at the ratios of 0, 22, and 112 metric tons/hectare, were used. The soils were air-dried, ground, and sieved to pass a 2-mm sieve. Some straw material remained. Extractant and 0.5 mL of chloroform (added to prevent microbial activity) were added to the soil, the mixtures were shaken overnight and centrifuged at 30000 rpm for 40 min, and the supernatant was removed. $Cu(NO_3)_2$ (pH adjusted to 6) was added to each of 10 30-mL aliquots of the extract to give total Cu concentrations ranging from 1 ppb to 10 ppm. Solutions were shaken for 1 h after addition of the copper prior to analysis.
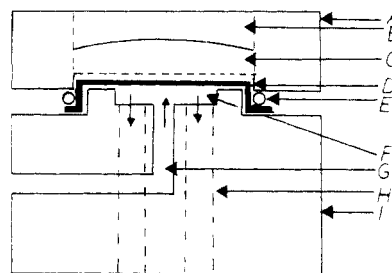
Figure 1. Schematic of the equilibration cell, adapted from Lampert (10). Teflon blocks (a and i) were machined to make substrate cell (f) and acceptor cell (b) cavities. The volume of the substrate cell (0.0097 cm^3) is defined by the 1.27 cm i.d. and 0.0076 cm height of the hole. The volume of the acceptor cell (0.635 cm radius) is defined by 0.2 mL of acceptor solution (c) resting on a Nafion 125 cation exchange membrane (d). The membrane is held in place by a Kel F ring (e) and has an exposed area of 1.27 cm^2. The substrate volume is continuously replaced by solution flowing in from a reservoir via a $^1/_{16}$ in. center entrance hole (g) and exiting by 6 radially distributed $^5/_{32}$ in. diameter holes (h).,

Donnan Equilibrium (DEq) Instrument Design. The cell, constructed by Lampert (10), is shown in Figure 1. Pumping was achieved with a 10-channel peristaltic pump (Masterflex 6568 pump drive, 7017 pump heads) operated at 65 mL/min. The height of the 0.2-mL acceptor solution over the membrane was 0.157 cm.

Membrane Preparation. The Nafion 125 (Du Pont) membranes were washed in 8:1:1 water–concentrated HCl–MeOH, followed by water rinses, and four subsequent equilibrations in 0.01 M $Sr(NO_3)_2$ for 1–3 h on a shaker. Currently available Nafion 117 is thicker than Nafion 125 (7 vs 5 mL), contains a larger number of active sites, and exhibits a greater degree of swelling. The overall conductivities are expected to be similar. However, it should be noted that the equilibration times for Nafion 117 may be different than those reported here.

GFAA Analysis. Analyses for total and free Cu^{2+} and Cd^{2+} were made by GFAA measurements on the substrate and acceptor solutions, respectively. A P.E. 2100 graphite furnace control unit on a P.E. 503 AA was used. Triplicate measurements were made. Standard curves were run before and after every set of 10 samples. The standard curves remained constant for up to 300 burns. The working limits of detection were in good agreement with instrument specifications (Cu^{2+}, ±1 ppb; Cd^{2+}, ±0.025 ppb). Linear standard curves with correlation coefficients >0.99 were obtained for both the Cd^{2+} and Cu^{2+} samples. A double peak was obtained for Cd^{2+} in $Sr(NO_3)_2$ reagents. The height of the first peak was unaffected by the presence of the second peak and corresponded to Cd^{2+} as determined by standard addition. The height of the first peak was measured by using 4-s atomization times. Ta coated tubes were used.

ISE Measurements. The donor solutions were analyzed for Cu^{2+} by using an Orion ISE in conjunction with an Orion double junction reference electrode with an Orion digital ionalyzer, Model 801A.

RESULTS AND DISCUSSION

Equilibration times were determined from sample solutions of 2.5 ppb $Cd(NO_3)_2$ and $Cu(NO_3)_2$. In Figure 2, the concentration of the acceptor solution as a percent of the total metal in the initial sample solution is plotted as a function of time. One hour was required to equilibrate the cation across the membrane. Presaturating the membrane in either $Cd(NO_3)_2$ or $Cu(NO_3)_2$ had no effect on speeding up the equilibration time. The sample solution concentration remains constant with time indicating that the measurement process does not disturb the solution, as expected from the volumes of the substrate and acceptor solutions, 0.2 and 40 mL, respectively. One hour was the maximum time obtained for a range of Cd^{2+} and Cu^{2+} concentrations from 2 ppb to 6 ppm. Equilibrations from samples of soil extracts followed the same time dependence although the final concentration within the acceptor solution was less than that in the sample solution.
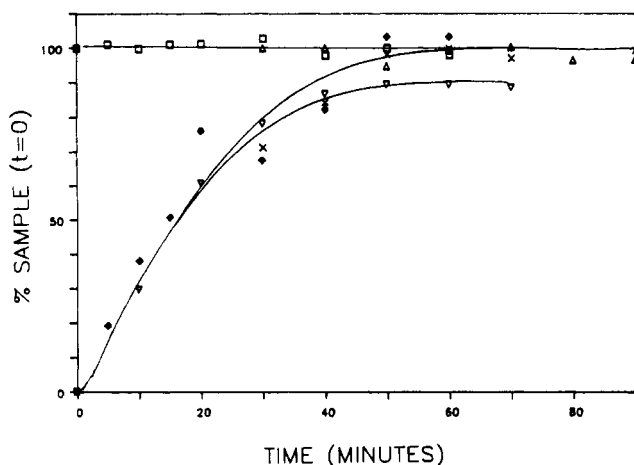
Figure 2. Time dependence of the acceptor and substrate solution concentrations as a percent of the initial (0 min) sample concentration: Cu 2.5 ppb sample ($\square$); Cu acceptor solution ($\blacklozenge$); Cd 2.5 ppb sample ($\triangle$); Cd acceptor solution ($\times$); Cd in 1:5 soil–0.01 M $Sr(NO_3)_2$ extract of 112 metric tons/hectare sludge-amended Plano silt loam (∇).

Table I. Comparison of Donnan Equilibrium/Graphite Furnace Atomic Absorption and Ion Selective Electrode Analyses for Cu^{2+} (pCu^{2+}) in Plano Silt Loam Extracted at 1 g of Soil/2 g of 0.01 M $Sr(NO_3)_2$

22 tons of sludge/ha		112 tons of sludge/ha	
ISE	DEq/GFAA	ISE	DEq/GFAA
7.8	7.0	a	7.5
6.0	5.8	a	7.4
4.7	4.6	6.8	6.5
4.5	4.4	4.6	4.6
4.1	4.2	4.1	4.1

a ISE values unstable.

As a result, all subsequent measurements were based on a 1-h equilibration time. The results are in agreement with those obtained by Lampert using radiotracer techniques (10). These results indicated that the method works for sample solutions within a simple matrix.

To ascertain if the steady-state concentration observed in the acceptor solution for the soil extract samples (Figure 2) is a reflection of the cationic concentration, DEq/GFAA measurements were compared to ISE measurements. Ion selective electrodes can be used to validate the results in the upper concentration regime in these types of matrices (19–22). A comparison of the two methods is given in Table I. There is good agreement between the two methods in the regime where ISE works best ($[Cu^{2+}] > 10^{-6}$). These results indicate that, in the upper concentration region, the DEq/GFAA method is reliable in the presence of a complex matrix such as an extract of a sludge-amended soil. This suggests that the 0.01 $Sr(NO_3)_2$ matrix is sufficient to match the substrate and acceptor solution electrolyte compositions in the presence of the sludge amendments. In addition, the values obtained for the amounts of copper in the amended and unamended soils are consistent with literature reports. The total metal in the extracts increased from the unamended soil ($pCd_T = 8.23$ and $pCu_T = 7.00$) to the 112 metric ton amended soil ($pCd_T = 6.8$ and $pCu_T = 5.2$). The free Cu^{2+} and Cd^{2+} in the sludge-amended soil were pCd^{2+} of 6.84 and pCu^{2+} unmeasurable. This indicates that Cd^{2+} is weakly complexed while Cu^{2+} is strongly complexed, which is consistent with published reports (9).

On the basis of these preliminary studies, estimates of soil solution complexing capacities were made. Representative titration curves are given in Figure 3. For the unamended
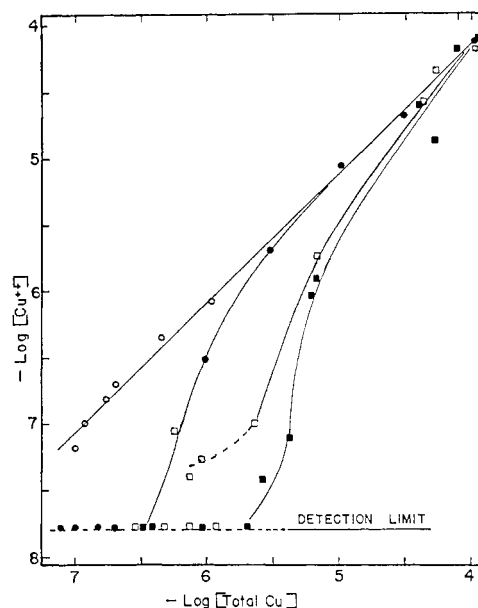
Figure 3. Titration curves of soil solution extracts with copper plotted as total copper vs free or cationic copper as determined by DEq/GFAA: (——) detection limit of the GFAA; (O) 0 metric tons sludge/hectare amended soils extracted at a ratio of 1:2 (weight soil:weight of 0.01 M $Sr(NO_3)_2$; ($\blacksquare$ and $\square$) 22 and 112 metric tons of sludge/hectare amended soils extracted at a ratio of 1:2; ($\bullet$) 112 metric tons of sludge/hectare amended soil extracted at 1:25 ratio.

soil there was a linear relationship (slope = 1.1 and correlation coefficient of 0.996) between the total and cationic amount of copper, indicating that the soil extract had few soluble ligands. As the sludge amendment ratio increased to 22 and 112 metric tons/hectare, discernible end points were observed. Note that the ISE measurements would fail to identify the end points since the detection limit for ISE is $[Cu^{2+}] > 10^{-6}$. Once the end point is passed, the various lines converge upon that of the unamended soil, as expected, as additional increments of copper added in excess of the complexation capacity should increase the cationic concentration.

Two trends in the data were observed (Figure 3): (1) As the extraction volume decreases by 10-fold, the end point of the titration also shifted by a factor of 10. This implies that the total amount of extractable ligands is fixed so that the concentration is dependent upon the extraction volume. (2) The end points shifted to larger total copper concentrations with increasing sludge amendment. The total ligand complexation capacity for the 1:2 soil/solution extract ratio of the 112 metric ton of sludge/hectare was 5×10^{-6} M as compared to 2×10^{-6} M for the 1:2 soil/solution extract ratio of the 22 metric ton sludge/hectare. These determinations of the ligand concentration are lower than those determined by either ion exchange or solvent extraction (10^{-4} M) (4, 8). Four reasons can be put forward for the disagreement. (a) The DEq/GFAA, ion exchange, and solvent extraction methodologies are equally accurate and the disagreement reflects the variation in soil samples. (b) In the ion exchange and solvent extraction methods the lability of the metal complexes can affect the total copper concentration measured as free copper. (c) The electrolyte used in DEq/GFAA (0.01 M $Sr(NO_3)_2$) is too low to be in excess of the natural electrolyte concentration in sludge-amended soils, despite our results showing agreement between the ISE and DEq/GFAA methodologies. In this case, the acceptor electrolyte concentration is smaller than the substrate electrolyte concentration, so $[Cu^{2+}]$ would be underestimated and, therefore, [L] could be overestimated. (d) Some strongly complexed metal equilibrates across the membrane. This would tend to overestimate $[Cu^{2+}]$ and hence underestimate [L]. Further studies will compare all of the

various methodologies for a single soil sample.

In summary, these results indicate that DEq/GFAA is a promising method for measuring soil solution extract complexation capacities.

LITERATURE CITED

(1) Bertha, E. L.; Chopin, G. R. *J. Inorg. Nucl. Chem.* **1979**, *40*, 655–658.
(2) Choppin, G. R.; Nash, K. L. *J. Inorg. Nucl. Chem.* **1981**, *43*, 357–359.
(3) Nash, K. L.; Choppin, G. R. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1045–1050.
(4) Miller, M. H.; Ohlrogge, A. J. *Soil Sci. Soc. Am. Proc.* **1958**, *20*, 225–228.
(5) Hodgson, J. F.; Geering, H. R.; Norvell, W. A. *Soil Sci. Soc. Am. Proc.* **1965**, *28*, 665–669.
(6) Hodgson, J. F.; Lindsay, W. L.; Trierweiler, J. F. *Soil Sci. Soc. Am. Proc.* **1966**, *30*, 723–726.
(7) Geering, H. R.; Hodgson, J. F. *Soil Sci. Soc. Am. Proc.* **1969**, *33*, 54–59.
(8) Crosser, M. L.; Allen, H. E. *Soil Sci.* **1977**, *123*, 176–181.
(9) Fitch, A.; Stevenson, F. J. 1986 In *Interactions of Soil Minerals with Natural Organics and Microbes*; Soil Science Society of America, Special Publication 17; Soil Science Society of America: Madison, WI, 1986; pp 29–58.
(10) Lampert, J. K. Ph.D. Thesis, University of Wisconsin—Madison, 1982.
(11) Minnich, M. M.; McBride, M. B. *Soil Sci. Soc. Am J.* **1987**, *51*, 568–572.
(12) Blaedel, W. J.; Christensen, E. L. *Anal. Chem.* **1967**, *39*, 1262–1265.
(13) Blaedel, W. J.; Haupert, T. J.; Evenson, M. A. *Anal. Chem.* **1969**, *41*, 583–590.
(14) Cox, J. A.; Kuo-Hsien, C. *Anal. Chem.* **1978**, *50*, 601–602.
(15) Cox, J. A.; Twardowski, Z. *Anal. Chem.* **1980**, *52*, 1503–1505.
(16) Cox, J. A.; Olbrych, E.; Brajter, K. *Anal. Chem.* **1981**, *53*, 1309–1311.
(17) Cox, J. A.; Gajek, R.; Litwinski, G. R.; Carnahan, J., Trochimczuk, W. *Anal. Chem.* **1982**, *54*, 1153–1157.
(18) Cox, J. A.; DiNunzio, J. E. *Anal. Chem.* **1977**, *49*, 1272–1275.
(19) Murrman, R. P.; Koutz, F. R. Special Report 171, U.S. Cold Regions Research & Engineering Lab, Hanover, NH, 1972; pp 48–74.
(20) Cavallaro, N.; McBride, M. B. *Soil Sci. Soc. Am. J.* **1980**, *44*, 881–882.
(21) Cavallaro, N.; McBride, M. B. *Soil Sci. Soc. Am. J.* **1980**, *44*, 729–752.
(22) Fitch, A.; Stevenson, F. J.; Chen, Y. *Org. Geochem.* **1986**, *9*, 109–116.

Alanah Fitch*

Department of Chemistry
Loyola University of Chicago
6525 North Sheridan Road
Chicago, Illinois 60626

Philip A. Helmke

Department of Soil Science
University of Wisconsin
Madison, Wisconsin 53706

Influence of the Vessel Materials and Solvents on the Stability of Mixtures of Bis(2,4,6-trichlorophenyl) Oxalate and Hydrogen Peroxide for Peroxyoxalate Chemiluminescence

Sir: The peroxyoxalate chemiluminescence (PO-CL) method has been widely acknowledged as an ultrasensitive detection technique in high-performance liquid chromatography (HPLC) (*1*) and flow injection analysis (*2*). The greatest advantage of this technique is that extremely high sensitivity can be attained with a very simple detection device. For example, subfemtomole levels of Dns-amino acids were measured by HPLC with a PO-CL detector consisting of a simple flow cell placed in front of a photomultiplier tube (*3*).

One problem in the application of this method to an actual detection system is that many factors can affect the intensity and/or the lifetime of PO-CL reactions and, consequently, make the response of the detector unstable. These factors also make it difficult to determine the optimum conditions for measurements of the highest sensitivity. Therefore, we have focused our efforts on elucidating the sources of disturbance. In a previous paper (*4*), we discussed the measuring conditions that influence the intensity and the lifetime of PO-CL reactions. In this communication, we report on two other factors that can cause deterioration in the stability of a mixture of oxalate and H_2O_2, the materials of the reservoir bottles and the solvents.

In 1967, Rauhut et al. measured the deactivation rate of the mixture of bis(2,4-dinitrophenyl) oxalate (DNPO) and H_2O_2 dissolved in dimethyl phthalate and determined the half-life to be ca. 70 min, but they did not mention what type of material they used as a reservoir for the solution (*5*). Sigvardson and Birks referred to the decomposition of bis-(2,4,6-trichlorophenyl) oxalate (TCPO) in their 1983 paper (*6*). They found that TCPO in acetone stored in an amber soda-lime glass bottle decomposed by half in 6 h, but was quite stable in a borosilicate glass bottle.

In this work, we measured the dependence of the decomposition rates of TCPO and the deactivation rates of $TCPO/H_2O_2$ mixtures on the reservoir materials and the solvents. We observed the highest rate of deactivation of a $TCPO/H_2O_2$ mixture in acetone stored in soda-lime glass bottles. It was stable in a Pyrex or sodium borosilicate glass bottle or a Teflon vessel when acetonitrile was used as a solvent. The cleaning procedure of the reservoirs also affected the deactivation rates of the mixture. From the results of these experiments, it was suspected that metal oxides contained in soda-lime glass caused the deactivation, and their influence was also measured. In every combination of the reservoir material and the solvent, the TCPO solutions were quite stable.

EXPERIMENTAL SECTION

The materials of the reservoir bottles tested were clear soda-lime glass, amber soda-lime glass, Pyrex borosilicate glass, sodium borosilicate glass, Teflon, and stainless steel. Solvent effects were measured in acetonitrile, acetone, or ethyl acetate.

A bottle of each material was purchased from American Scientific Products, McGaw Park, IL. All the chemicals were the same as those in the previous paper (*4*) or of reagent grade.

Cleaning Procedure of the Vessels. Two procedures were tested. (1) The vessels were soaked in a solution of detergent (MICRO, International Products Corp., diluted according to the manufacturer's instructions) for at least 1 day and rinsed with water purified by the Barnstead NANOpure II system (Sybron Barnstead, Boston, MA). (2) After procedure 1, the vessels were soaked in 1 M NaOH and 1 M HNO_3 solutions in turn for 1 day each and rinsed with purified water.

Measurements of the Decomposition of TCPO. The same HPLC system as that in the previous report (*4*) was used. The compositions of all the solutions including the sample were also