

rectangular channel-type flow-through electrodes to the conditions employed in this study, the hydrodynamic diffusion layer thickness during deposition is estimated to vary from zero at the upstream end of the electrode to  $1.2 \times 10^{-3}$  cm at the downstream end. Use of the nylon insert increases the linear velocity of solution passing through the electrode, reducing the hydrodynamic diffusion layer thickness and giving rise to more effective mass transfer by convective diffusion. The thickness of the flow layer is a compromise between efficiency of mass transport (12) and reliability with which the nylon insert can be extracted from the tubular electrode without removing deposited analyte. Experiments carried out at extended deposition times suggest that, under the conditions of the present study, ca. 50–60% of the Hg(II) in solution is deposited after 5 min. For the determination of mercury, the accuracy, precision, and sensitivity of the EDAA technique are comparable to that obtained by the gold trap/cold vapor method (7). In our hands, however, the EDAA method reduces the time required for inorganic mercury determination

by ca. 50%. The flow cell should find application for the determination of other trace metals by EDAA.

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## Formation Constant of $\beta$ -12-Molybdosilicate in Acidic Media

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Silicate is determined in many laboratories by reaction with molybdate in dilute acid solution to form the heteropoly anion, 12-molybdosilicate (12-MSA) (1). The absorbance of the yellow 12-MSA can be related to the silicate concentration directly or the heteropoly anion can be reduced to form a heteropoly blue species. The formation of 12-MSA has been the subject of several previous studies. Strickland (2–4) was the first to report the formation of two 12-MSA isomers, the  $\alpha$  and  $\beta$  forms. The  $\beta$  isomer is that normally formed in analytical procedures, although the  $\alpha$  isomer is the thermodynamically stable form (2). The  $\alpha$  isomer is of  $T_d$  symmetry and has the structure originally proposed by Keggin (5). The structure of the  $\beta$  isomer of 12-tungstosilicate has been determined (6). It corresponds to a modification of the Keggin structure in which three Mo–O octahedra are rotated by  $60^\circ$  with respect to the rest of the molecule, reducing the symmetry to  $C_{3v}$ . Raman spectra of the  $\beta$  isomer of 12-MSA are consistent with this modified Keggin structure (7). The redox properties of the 12-MSA isomers upon gradual chemical and electrochemical reduction have been determined (8), and the pH-dependent decomposition of the  $\alpha$  isomer of 12-MSA has been studied by Raman spectroscopy (9). Several workers have investigated the kinetics of formation of the 12-MSA isomers (10, 11). The chemical findings on the formation of 12-MSA have led to silicate procedures that are precise and accurate (12, 13).

Despite these extensive studies, the formation constants of the 12-MSA isomers have not been previously reported. We have determined the conditional formation constant of the  $\beta$  isomer of 12-MSA at pH 1.2 and a molar ionic strength of 1.0 by Job's method of continuous variations. In contrast to the formation of molybdophosphates where three molybdophosphate species were postulated to explain the continuous variations data (14), one molybdosilicate equilibrium satisfactorily explains the continuous variations curves at several total silicate plus molybdate concentrations. Knowledge of the conditional formation constant of  $\beta$ -12-MSA should aid in optimization of silicate procedures to achieve high sensitivity.

### EXPERIMENTAL SECTION

Continuous variations studies were carried out at constant pH in three acidic media ( $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ). The total molar silicate and molybdate concentration ( $C_S + C_M$ ) was varied between 0.01 and 0.05 M but was held constant within each series of solutions as the mole fraction of silicate ( $X_S$ ) was varied. The molar ionic strength was adjusted to 1.0 by addition of the appropriate amount of  $\text{NaClO}_4$ . The required amounts of acid to adjust the solution pH to the specified value and the required amounts of  $\text{NaClO}_4$  to adjust the ionic strength were calculated on a CDC Cyber 760 computer with the HALTAFALL computer program (15). Equilibrium constants for the predominant Mo(VI) species in dilute acid solutions at 1.0 M ionic strength (16) were supplied to the program along with mass balance expressions for  $\text{H}^+$  and Mo(VI). Once the conditional formation constant was determined from one set of data, HALTAFALL was used to predict  $\beta$ -12-MSA concentrations for other data sets.

Stock solutions of  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaClO}_4$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  were prepared from the reagent grade chemicals without further purification and stored in polyethylene bottles. The acids were standardized by titrations with previously standardized NaOH solution. The silicate solution was standardized immediately with the  $\text{HNO}_3$  solution (bromocresol red end point) in order to avoid  $\text{CO}_2$  contamination from the air and additional silicate contamination from the glassware.

Absorbance measurements were made with a modular UV-visible spectrophotometer (GCA McPherson EU-700 series); the sample cell compartment was modified to house a brass, thermostated cuvette block (17) and a water-driven magnetic stirrer (G. F. Smith, Co.). The temperature of the cuvette block, cuvette, and solution was maintained at  $25.0 \pm 0.1^\circ\text{C}$  by circulating water from a constant temperature bath through the cuvette block. Absorbance measurements were made at 410 and 430 nm (monochromator spectral band-pass of 4 nm) where 12-MSA absorbs strongly and the Mo(VI) background absorption is small.

### RESULTS AND DISCUSSION

A plot of one set of continuous variations data for the formation of  $\beta$ -12-MSA is shown in Figure 1. The absorbance change at 430 nm ( $\Delta A_{430}$ ) is a maximum at a silicate mole fraction  $X_S$  of 0.077, which corresponds to a 12:1 mole ratio of molybdate to silicate. Continuous variations studies were

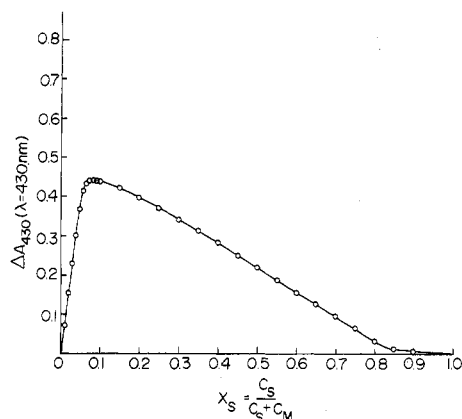


Figure 1. Continuous variations plot for 12-MSA formation in  $\text{HNO}_3$  at pH 1.2, ionic strength 1.0 M, and  $T = 25^\circ\text{C}$ ;  $C_M + C_S = 0.01\text{ M}$ .

Table I. Conditional Formation Constants of  $\beta$ -12-MSA at pH 1.2,  $I = 1.0\text{ M}$ , and  $T = 25.0^\circ\text{C}$

acid medium	$\log K_f'$ <sup>a</sup>	acid medium	$\log K_f'$ <sup>a</sup>
$\text{HNO}_3$	32.2	$\text{H}_2\text{SO}_4$	31.6
$\text{HClO}_4$	31.9		

<sup>a</sup> Uncertainties in  $\log K_f'$  values are estimated to be  $\pm 0.5$ .

also carried out with different total concentrations of silicate and molybdate,  $C_S + C_M$ , and with absorbances measured at 410 nm. All continuous variations plots had a similar shape to that shown in Figure 1. Within experimental error all plots had a maximum absorbance change at a 12:1 mole ratio of molybdate to silicate.

Because of the identical results at two different wavelengths and several different total  $C_S + C_M$  values, we conclude that  $\beta$ -12-MSA is the only molybdosilicate species that forms at pH 1.2.

The formation constant was calculated in the following manner. From the linear increase in  $\Delta A$  with  $C_S$  at low mole fractions of silicate (see Figure 1), it was concluded that essentially all the silicate present was converted to  $\beta$ -12-MSA for  $X_S \leq 0.02$ . The slope of the  $\Delta A$  vs.  $C_S$  plot under these conditions yielded the molar absorptivity  $\epsilon$  of  $\beta$ -12-MSA ( $r_{xy}$  values typically were 0.9998). Equilibrium  $\beta$ -12-MSA concentrations were then calculated from measured  $\Delta A$  values near the maximum in the continuous variations plot ( $0.07 < X_S < 0.10$ ). The conditional formation constant  $K_f'$  was then calculated from

$$K_f' = \frac{[\beta\text{-12-MSA}]}{[\text{Si}(\text{OH})_4][\text{Mo}(\text{VI})]^{12}} = \frac{[\beta\text{-12-MSA}]}{(C_S - [\beta\text{-12-MSA}])(C_M - 12[\beta\text{-12-MSA}])^{12}}$$

Results for the  $K_f'$  values in  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$  are shown in Table I. These values are conditional constants at pH 1.2 and 1.0 M ionic strength. From the variances in the  $\Delta A$  measurements and the value of  $\epsilon$  obtained, we estimate from a propagation of error analysis that the experimental error in  $\log K_f'$  values is  $\approx \pm 0.5$ .

To test how well the calculated  $K_f'$  values describe the entire continuous variations curves, we calculated  $\beta$ -12-MSA concentrations at each  $X_S$  value and compared the results to the measured values of  $\Delta A$ . A proportional relationship (constant  $\epsilon b$  value) over the entire range of  $X_S$  values would indicate excellent agreement. For one data set in  $\text{HNO}_3$  the results are shown in Table II. If the point at  $X_S = 0.90$  is neglected

Table II. Comparison of Calculated  $\beta$ -12-MSA Concentrations with Experimental Absorbances<sup>a</sup>

$X_S$	$[\beta\text{-12-MSA}]$ , mM	$\Delta A_{430}$	$\epsilon b$ , $\text{M}^{-1}$
0.01	0.100	0.073	730
0.02	0.200	0.152	760
0.03	0.300	0.222	740
0.04	0.400	0.292	730
0.05	0.499	0.373	747
0.06	0.564	0.400	709
0.07	0.577	0.411	712
0.08	0.578	0.414	716
0.09	0.575	0.405	704
0.10	0.571	0.401	702
0.15	0.542	0.393	725
0.20	0.507	0.368	726
0.25	0.470	0.351	747
0.30	0.433	0.324	748
0.40	0.356	0.263	739
0.50	0.279	0.210	753
0.60	0.201	0.167	833
0.70	0.125	0.104	832
0.80	0.052	0.037	702
0.90	0.001	0.001	1000

<sup>a</sup>  $\text{HNO}_3$ , pH 1.2,  $I = 1.0\text{ M}$ ,  $T = 25.0^\circ\text{C}$ ,  $\log K_f' = 32.2$ ,  $C_S + C_M = 0.01\text{ M}$ .

(it is  $7\sigma$  from the mean), the average and standard deviation of the  $\epsilon b$  value are  $740 \pm 37$  (relative standard deviation = 5%). Similar correspondence was obtained for all three acidic media and for the different total  $C_S + C_M$  values. We thus conclude that a single equilibrium with the conditional formation constants given in Table I adequately describes the formation of  $\beta$ -12-MSA.

We attempted to determine the pH dependence of the  $K_f'$  values by obtaining continuous variations data at pH 1.6 and pH 2.0. However, significant amounts of the  $\alpha$  isomer were found at pH values higher than 1.8 as noted by an apparent decrease in the molar absorptivity of  $\beta$ -12-MSA with increasing pH. These results are consistent with the observations of other workers (10). We also attempted to determine the formation constant of the  $\alpha$  isomer at pH 3.6. However, the lower molar absorptivity of the  $\alpha$  isomer in comparison to that of the  $\beta$  isomer led to uncertainties in the  $K_f'$  values that spanned several orders of magnitude.

Some interesting similarities and differences exist between these results and those for the corresponding molybdophosphate system (14). The conditional formation constants for  $\alpha$ -12-MSA at pH 1.2 in all the acidic media are of the same order of magnitude as those for 12-molybdophosphate (12-MPA) at pH 0.6 in  $\text{HNO}_3$  and  $\text{HClO}_4$  (one should note that the ionic strength was 3.0 M in the 12-MPA study). In addition, the molar absorptivity for  $\beta$ -12-MSA at 430 nm is within 15% of the molar absorptivity for 12-MPA at the same wavelength (again, ionic strengths were different in the two studies). On the other hand, the optimum pH for forming 12-MSA is higher than that for forming 12-MPA. The  $\beta$ -12-MSA formation constant is nearly independent of the type of acid used to adjust the pH, whereas the formation constant of 12-MPA is much lower in  $\text{H}_2\text{SO}_4$  than in  $\text{HClO}_4$  and  $\text{HNO}_3$  (14). Apparently the degree of complexation of sulfate with Mo(VI) or with the heteropoly anion is much less in the 12-MSA case because of the smaller total sulfate concentration.

The  $\beta$ -12-MSA species appears to be the only molybdosilicate species formed at pH 1.2. As a consequence stoichiometric amounts of  $\beta$ -12-MSA can be formed from silicate and molybdate when the mole fraction of silicate is less than 0.02 (see Table II). Because the molybdophosphate system is influenced by equilibria among three species (14), only 20–80% of the available phosphate is converted to 12-MPA

at mole fractions of phosphate <0.02.

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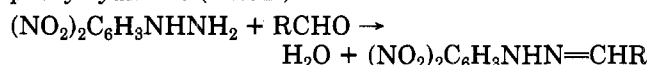
## Collection Efficiencies of Cartridges and Microimpingers for Sampling of Aldehydes in Air as 2,4-Dinitrophenylhydrazones

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The determination of low levels (typically parts per billion) of formaldehyde and other aldehydes and ketones in air is of importance in a number of areas of pollution control including indoor pollution, industrial hygiene, characterization of industrial effluents, modeling of ozone and other photochemical oxidants, and research in atmospheric photochemistry. However, due to a large extent to the limitations inherent to the analytical methods employed to date, there is a paucity of data concerning levels of carbonyls in the air environment (1).

Recently, several investigators have applied high-performance liquid chromatography (HPLC) to the determination of formaldehyde (2-9) and of other carbonyls (3, 4, 7-9) in polluted atmospheres. This method entails the selective reaction of airborne carbonyls with the reagent 2,4-dinitrophenylhydrazine (DNPH)



and the subsequent separation and quantitation of the corresponding 2,4-dinitrophenylhydrazones by HPLC. Several sampling devices have been employed, including microimpingers containing DNPH solutions (3, 4, 7-9), cartridges with DNPH coated on a solid support (6, 10), cryogenic concentration (11), and DNPH solutions in rotating flasks (5).

In spite of the critical importance of establishing the collection efficiency (CE) of these DNPH-sampling devices, there is virtually no information concerning CE studies in the range of concentrations and conditions directly relevant to atmospheric sampling. In this study, we have investigated the collection efficiencies of several cartridges and microimpingers for three representative carbonyls, formaldehyde, acetaldehyde, and benzaldehyde. Parameters studied included aldehyde concentration, sampling volume, time and flow rate, matrix air humidity, and addition of organic solvents to the aqueous DNPH reagent.

### EXPERIMENTAL SECTION

Cartridges consist of 100 mm long  $\times$  6 mm i.d. glass tubes packed with 20 mesh, HF-etched glass beads impregnated with DNPH reagent. The DNPH reagent consists of aqueous, acidic ( $\text{H}_3\text{PO}_4$ ) saturated solutions of DNPH to which small amounts of poly(ethylene glycol) are added. The glass beads are immersed in the DNPH reagent, and the water is slowly evaporated. The

purpose of adding poly(ethylene glycol) is to promote the formation of a viscous film on the bead surface. Once packed with glass beads and plugged with glass wool, the cartridges are sealed with plastic caps and stored in the dark at refrigerator temperature prior to sampling and prior to extraction and HPLC analysis.

Microimpingers (e.g., Kontes No. K737550 midjet impingers) contain 10 mL of aqueous, acidic (2 N HCl) DNPH reagent to which 10 mL of an HPLC-grade organic solvent can be added. Organic solvents employed to date include *n*-hexane and a 9:1 by volume mixture of cyclohexane and isooctane. Storage prior to and after sampling is in the dark at refrigerator temperature. Blanks are included in each batch of cartridges and impingers prepared and are subjected to the same handling and analytical protocol employed for the actual samples.

Collection efficiency studies are carried out by using a dynamic dilution system. Mixtures of  $\sim 1$  torr of the carbonyl to be studied (as measured by a 0-20 torr Wallace and Tiernan absolute pressure gauge) in  $\sim 780$  torr of  $\text{O}_2$ ,  $\text{N}_2$ , or purified air, are prepared in a 22-L Pyrex bulb. After allowing 1-3 h to ensure complete mixing, these mixtures are diluted in a flow system using calibrated rotameters and capillary flow meters. Carbonyl concentrations of 100-300 ppb in the diluent gas are typically employed. After  $\sim 1$  h of flowing this mixture at a flow rate of  $\sim 5$  L/min, sampling is initiated. Samples are typically collected at a sampling flow rate of  $1.0 \pm 0.2$  L/min, and the volume sampled is monitored by a wet test gas meter connected to the exit of a Metal Bellows sampling pump.

The diluent gas stream can be humidified to  $\sim 40$ -50% relative humidity by passing this diluent gas stream through a bubbler containing distilled water.

Formaldehyde is prepared by heating paraformaldehyde ( $>95\%$  purity) at 373 K under vacuum and passing the effluent gases through a methanol/liquid-nitrogen slush trap (179 K) to remove  $\text{H}_2\text{O}$  and possible disproportionation products, and formaldehyde is collected in a trap at 77 K. Acetaldehyde is degassed under vacuum and distilled into an ethanol/liquid nitrogen slush trap (156 K) and thence to a liquid nitrogen trap (77 K) under vacuum. Benzaldehyde is degassed under vacuum.

Cartridge and impinger samples were analyzed by HPLC as described by Fung and Grosjean (2). Reference 2 could be consulted for a more detailed description of the analytical method and of its quantitative aspects including reproducibility, calibration, and nanogram detection limits.

### RESULTS AND DISCUSSION

Our studies included five collection devices (two cartridges and three impingers), three diluent gases ( $\text{O}_2$ ,  $\text{N}_2$ , and air),