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APPLICATION OF MOLECULAR SUBSTITUENT PARAMETERS FOR THE SPECIATION OF TRACE ORGANOMETALS IN ENERGY-RELATED PROCESS FLUIDS BY ELEMENT-SELECTIVE HPLC

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High performance liquid chromatographic separations coupled with element-selective detectors provide trace molecular speciation methods applicable to energy-related process fluids and associated waste leachates. These materials present a challenge because they contain complex matrices whose chemistries are not well understood, and the processes have the potential to generate compounds containing toxic metals and metalloids that are either unexpected or have not been previously identified. Consequently, the ability to reliably ascertain the molecular structures of such unknown substances by relatively simple measurements of their chromatographic retention properties is very desirable. Our present work shows a linear correlation of the logarithm of the chromatographic capacity factor with the linear sum of the appropriate structural substituent parameters for a number of organoarsenicals, separated by an ion-exchange mechanism, and a number of organotins, separated by a hydrophobic mechanism. An illustration of the application of this linear free energy relationship as a diagnostic in the separation of trace organoarsenicals, by ion-exchange chromatography, was performed on the analysis of process waters from oil shale retorting and on leachates from raw oil shale.

Key words: Atomic absorption; energy-related process fluids; leachate; linear free energy; liquid chromatography; molecular substituent; oil shale; organoarsenic; organotin; retention index; speciation.

1. Introduction

1.1 Trace Element Speciation

The molecular characterization, or chemical speciation, of metal and metalloid species, at trace levels has provided valuable information in the areas of: the aquatic chemistry of trace metals [1]; the microbial transformations of trace metals [2,3]; the biochemistry of trace metals [4]; and the chemistry of controlled release biocides containing metals [5]. This information is not obtainable by total trace metal analysis [6].


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A widely used method for trace metal speciation is the chromatographic separation of the metal-containing compound, with element-selective detection in either on-line or off-line modes. This technique is capable of characterizing trace metal species in the presence of numerous other interfering compounds which may prohibit the use of many, if not all, direct spectroscopic identification techniques. Thus, chromatographic separations with element-selective detection have been and will be used extensively to characterize trace metal-containing compounds in the variety of complex matrices generated from energy-related processes [7-9]. In general, both gas and liquid chromatographic systems are used. Element-selective detectors are preferably used on-line, thereby minimizing sample handling, analysis time, and the time needed to optimize the chromatographic system. The element-selective detectors include: emission and atomic absorption spectroscopy, and electrochemical, and radioactivity detectors [10]. The technique relies upon the elution of the trace metal-containing compound with a retention time unique from all other compounds containing the trace metal under investigation, as determined by an authentic standard.

Gas chromatographic retention has been related to volatility, and that relationship has provided a useful index of retention, the Kováts Index [11]. In speciation studies involving liquid chromatographic separations, it would be useful to have a rational system based on thermodynamic properties, with due consideration of kinetic rates on the chromatographic time scale, in order to:

a. predict the retention of a sought after compound;

b. predict the possible structure(s) of unknown compounds from the experimentally determined retention times;

c. predict the possible co-elution of interfering compounds; and,

d. optimize chromatographic systems for the desired separation.

The relationship between structural substituent parameters and chromatographic retention has provided a starting point for such a system and has been applied to the separation of many organic compounds [11-13].

1.2 Structural Substituent Parameters

The electronic structural substituent parameter, $\sigma$, is based on the ionization of a derivative compound with respect to its parent compound. The determination of $\sigma$ is based on equation 1,

$$\rho\sigma = \log K_x - \log K_H \quad ,$$

where $K_x$ is equal to the ionization constant of the derivative compound, and $K_H$ is the ionization constant of the parent compound. The constant was first introduced by Hammett [14] in 1935, based on benzoic acid as the parent compound, with meta and para derivatives. In 1953, Jaffé et al. [15] published $\sigma$ values for aromatic phosphonic acids. In 1956,
Hastryukova and Kabachnik [16] published $\sigma^\theta$ values for the aqueous ionization of a large variety of substituted phosphorous acids.

The hydrophobic structural substituent parameter ($\pi$) is based on the partitioning of a derivative between octanol and water, with respect to the partitioning of its parent compound, expressed as,

\[ \pi_x = \log P_x - \log P_M, \]

where $P_x$ is the partition coefficient of the derivative and $P_M$ is the partition coefficient of the parent compound [17]. The hydrophobic (or lipophilic) parameter as well as the octanol-water partition coefficients have been applied to: the transport of compounds across biological membranes [18]; the chromatographic separation of organic compounds [12], including herbicides [19]; the correlation of the bioaccumulation of organic compounds in both fish and microbes [20,21]; and toxicological structure activity relationships [22].

1.3 Application of Molecular Substituent Parameters to Chromatographic Retention

Two publications have laid the foundation for the elucidation of the mechanisms of chromatographic separations, based on thermodynamic principles, as well as the prediction of liquid chromatographic retention. In 1949, Martin [13], while discussing theoretical aspects of partition chromatography, predicted that the addition of a substituent group to a parent compound would change the partition coefficient by a certain factor dependent upon the nature of the substituent group "but not on the rest of the molecule". Lederer [23], in 1957, reviewed the paper chromatographic applications of this principle to homologous series of compounds, differing only in the number of methylene groups, in relation to solvent selection and temperature variations.

In 1976, Horváth et al. [24] presented a model of solvophobic chromatographic separations based on thermodynamic principles. Chen and Horváth [25] then extended this work to determine quantitative structure-retention relationships, and Naham and Horváth [26] have evaluated octanol-water partition coefficients from chromatographic measurements. Baker [11] has developed retention indices for liquid chromatographic separations based on Hansch's $\pi$ parameter that are similar to Kováts Indices, used for gas chromatography. In these studies, the solutes were all biogenic organic acids and bases, and a wide variety of drugs. Other reports of quantitative structure-retention relationships for phenols [27] and herbicides [19] have been made.

The first application of thermodynamic principles to the chromatographic retention of organometal molecules involved the separation of di- and triorganotins by ion-exchange chromatography with atomic absorption detection. Jewett and Brinckman [28] demonstrated a linear relationship between the logarithm of the chromatographic capacity factor $k'$ and the $\sigma^\theta$ molecular substituent parameter, with a correlation coefficient of 0.992, based on
23 individual $k'$ values for five trialkyltin compounds, separated in water as the $R_3Sn^+$ cations.

2. Experimental

2.1 Instrumentation

The high-performance liquid chromatograph (HPLC) coupled with graphite furnace atomic absorption (GFAA) detector is illustrated schematically in Figure 1. For the separation of the arsenicals, the HPLC consisted of two dual-piston pumps, computerized chromatographic controller, high pressure mixing chamber, and an ultra-violet (UV) absorbance detector. The injection valve was equipped with a 200 $\mu$L sample loop. The GFAA spectrophotometer was equipped with an As electrodeless discharge lamp, a dual-channel recorder, for recording both UV absorbance and the histogrammic GFAA output, and a digital integrator for more accurately determining the GFAA output.

![Figure 1. Schematic of HPLC-GFAA system showing programmed solvent gradient flow and in-line UV and GFAA detectors [5,28]. The GFAA spectrophotometer consists of a heated graphite atomizer (HGA) and an atomic absorption spectrophotometer (AA).](image)

For the separation of the tetraorganotins, the HPLC employed a single piston pump (with pulse dampener) and a UV absorbance detector. The injection valve was equipped with a 20 $\mu$L sample loop. The GFAA unit was equipped with an electrodeless discharge Sn lamp. The data were collected on a dual channel recorder, and an integrator was used to digitize the GFAA output.

The experimental parameters for the two atomic absorption spectrophotometers used during this study are presented in Table 1.
2.2 Chromatographic Systems

The separation of the arsenicals was based on the work of Woolson and Aaronson [29]. The chromatographic column was a weak anion exchange column (3 mm x 250 mm). The gradient elution employed consisted of elution with 80:20 (vol.%)$ H_2O:MeOH$ initially for ten min, and a linear gradient of 5% min$^{-1}$ to 85:15 $H_2O:MeOH$ $[0.02$ M $(NH_4)_2CO_3]$. The separation of the organotins was accomplished under isocratic conditions using a $C_{18}$ (octadecylsilane) reversed bonded-phase column (10 μm particle size). The mobile phase employed was 93:7 (vol.%)$ methanol:H_2O$.

2.3 Reagents and Standards

The distilled water employed during this study was further purified using an exchange resin system to obtain 18 MΩ-cm resistivity. The methanol used for the separation of the arsenicals was spectrograde, while the methanol used for the separation of the organotins was chromatographic grade. The ammonium carbonate used was analyzed reagent grade. The arsenic standards employed were obtained commercially and from Profs. Irgolic and Zingaro (Department of Chemistry, Texas A&M University), whose generosity is greatly appreciated. The organotin compounds were either obtained commercially or synthesized in our laboratories.

3. Results and Discussion

3.1 Relationship Between Chromatographic Retention and Molecular Substituent Parameters

3.1.1 Separation of Arsenicals

The calculation of the $Z_0\phi$ values for the arsenic compounds chromatographed is simply the linear sum of the $\phi$ parameters of the individual molecular substituents, which

Table 1. Experimental GFAA Conditions

<table>
<thead>
<tr>
<th>AA Unit</th>
<th>Dual-pump HPLC-AA system</th>
<th>Single-pump HPLC-AA system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>As</td>
<td>Sn</td>
</tr>
<tr>
<td>Wavelength</td>
<td>193.7 nm</td>
<td>224.6 nm</td>
</tr>
<tr>
<td>Band-pass</td>
<td>0.7 nm</td>
<td>0.7 nm</td>
</tr>
<tr>
<td>Dry</td>
<td>20 s, 115 °C</td>
<td>20 s, 85 °C</td>
</tr>
<tr>
<td>Char</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Atomize</td>
<td>7 s, 2700 °C</td>
<td>7 s, 2700 °C</td>
</tr>
<tr>
<td>Integrate</td>
<td>Peak Ht, 8 s</td>
<td>Peak Ht 8 s</td>
</tr>
</tbody>
</table>
replace the ionic oxygen substituents in the parent compounds. The method for calculating the $\Sigma_0^\phi$ values is presented in Table 2; the parent compound is taken as the trisubstituted form of arsenate whose $\Sigma_0^\phi$ value is designated as 0, where $A = B = C = 0^-$. The ionic form of the derivative compound is very important because simple monoprotonation of the compound contributes -0.39 $\sigma^\phi$ unit to the total $\Sigma_0^\phi$ value of the derivative. In most cases, the ionic form of the derivative was determined by considering the pK$_a$ of the compound with respect to the pH of the eluting solvent. In the cases of dimethylarsinic acid and the diphenylarsinic acid, the neutral forms were considered in an attempt to obtain the best fit of the data. Considering the pK$_a$'s of these compounds, to ascribe these as neutral forms is not entirely satisfactory; however, there might be some non-additive electronic effects due to the presence of two organic substituents on the central arsenic atom.

Table 2. The Calculation of the $\Sigma_0^\phi$ for Organoarsenic Acids

<table>
<thead>
<tr>
<th>Parent Compound</th>
<th>$\Sigma_0^\phi = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^-$</td>
<td>$\sigma^\phi$ (Ref.16)</td>
</tr>
<tr>
<td>B/C</td>
<td></td>
</tr>
<tr>
<td>$-0^-$</td>
<td>0.00</td>
</tr>
<tr>
<td>$-\text{OH}$</td>
<td>-0.39</td>
</tr>
<tr>
<td>$-\text{Ph}$</td>
<td>-0.48</td>
</tr>
<tr>
<td>$-\text{CH}_3$</td>
<td>-0.96</td>
</tr>
</tbody>
</table>

The separation of the arsenicals, using the HPLC-GFAA system, is demonstrated in Figure 2. The non-response of the UV absorbance detector is to be noted with the exception of the chromophore 4-aminophenylarsonic acid. The histogrammic output of the GFAA signal results from the discrete sampling of the HPLC effluent limited by the drying, charring, atomization, and cooling cycle of the graphite furnace at approximately 45 s intervals [5].

The relationship between the natural logarithm of the chromatographic capacity factor for the arsenic compounds and the calculated $\Sigma_0^\phi$ values for these compounds is
Figure 2. UV and arsenic-specific AA chromatograms for an aqueous solution containing five organoarsenic acids and arsenate (as numbered) are compared. Complete separations of this and similar mixtures of other arsenicals were effected in comparable analysis times.

sent in Figure 3. The relationship is linear, with a correlation coefficient of 0.971 based on 111 data points. Similar linear relationships also were obtained using different non-linear convex and concave HPLC elution gradients. This linear relationship provides a method for: predicting the retention time of a sought after compound based on the calculated $\sigma^\phi$ value; predicting the co-elution of an interfering compound, based on the compounds which have a similar $\sigma^\phi$ value; and optimizing the desired separation by changing the chromatographic system to achieve the needed change in retention time for the difference in $\sigma^\phi$ values of the compounds to be separated.

3.1.2 Separation of Organotins

The method for obtaining the $\Sigma\pi$ values for the $R_4-nR'_nSn$ tetraorganotins used in this work is presented in Table 3. The $\Sigma\pi$ value for each neutral organotin molecule is simply calculated by the linear summing of the individual $\pi$ substituent parameters.

The separation of the organotins using the HPLC-GFAA system is demonstrated in Figure 4. The non-response of the UV-absorbance detector is to be noted, with the exception of the chromophoric dibutylphenyltin and the tetraethyltin. In the case of the tetraethyltin, the UV response possibly arises from the large column loading of this compound, due to the difficulty in detecting volatile compounds because of losses during the drying cycle of the GFAA.
The linear regression between \( \ln k' \) and \( \Sigma_0^\phi \) obtained on a weak anion exchange column (WAX) is shown for the following arsenicals: 1, \( \text{Me}_2\text{As}(0)\text{OH} \); 2, \( \text{Pe}_2\text{As}(0)\text{O}^- \); 3, \( \text{Ph}_2\text{As}(0)\text{OH} \); 4, \( \text{Me}_2\text{As}(0)\text{O}^- \); 5, \( \text{BuAs}(0)(\text{OH})\text{O}^- \); 6, \( \text{EtAs}(0)(\text{OH})\text{O}^- \); 7, \( \text{MeAs}(0)(\text{OH})\text{O}^- \); 8, \( (\text{4-NH}_2\text{Ph})\text{As}(0)(\text{OH})\text{O}^- \); 9, \( \text{PhAs}(0)(\text{OH})\text{O}^- \); 10, \( \text{AsO}(\text{OH})_2\text{O}^- \); 11, \( \text{As}(0)(\text{OH})\text{O}^- \); 12, \( (\text{4-NO}_2\text{Ph})\text{As}(0)(\text{OH})\text{O}^- \). The black circles indicate estimated \( \ln k' \) for alternate choices of protonated or deprotonated arsenic species not acceptable in the fit shown.

Table 3. The Calculation of \( \Sigma \pi \) for Tetraorganotins, \( R_4 - n R' n \text{Sn} \)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Solvophobic Parameter (( \pi )) [17]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH(_3)</td>
<td>0.56</td>
</tr>
<tr>
<td>-C(_2)H(_5)</td>
<td>1.02</td>
</tr>
<tr>
<td>-C(_3)H(_7)</td>
<td>1.55</td>
</tr>
<tr>
<td>-C(_4)H(_9)</td>
<td>1.53</td>
</tr>
<tr>
<td>-C(_6)H(_5)</td>
<td>2.13</td>
</tr>
<tr>
<td>-C(_6)H(_5)</td>
<td>1.96</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( R )</th>
<th>( R' )</th>
<th>( n )</th>
<th>( \Sigma \pi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>0</td>
<td>4 x 0.56 = 2.24</td>
<td></td>
</tr>
<tr>
<td>CH(_3)</td>
<td>C(_2)H(_5)</td>
<td>2</td>
<td>(2 x 0.56) + (2 x 1.02) = 3.16</td>
</tr>
<tr>
<td>C(_2)H(_5)</td>
<td>0</td>
<td>4 x 1.02 = 4.08</td>
<td></td>
</tr>
<tr>
<td>C(_3)H(_7)</td>
<td>0</td>
<td>4 x 1.53 = 6.12</td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_5)</td>
<td>C(_4)H(_9)</td>
<td>2</td>
<td>(2 x 1.96) + (2 x 2.13) = 8.18</td>
</tr>
<tr>
<td>C(_6)H(_5)</td>
<td>C(_4)H(_9)</td>
<td>1</td>
<td>(3 x 1.96) + 2.13 = 8.01</td>
</tr>
</tbody>
</table>
Figure 4. The isocratic separation of four tetraorganotins on an octadecyl-silane chemically bonded phase columns, using methanol: H₂O (93:7 vol.%) at a flow rate of 1.0 mL min⁻¹.

The relationship between the natural logarithm of the chromatographic capacity factor for the organotins and the calculated π values for these compounds is presented in Figure 5. The relationship for the alkyl and mixed alkyl derivatives is linear, with a correlation coefficient of 0.989, based on 41 data points. The relationship for the mixed butyl-phenyl organotins is also linear, with a correlation coefficient of 0.989, based on 31 data points, but with a much larger slope. The difference in behavior between the alkyl and phenyl derivatives is possibly due to steric, electronic, or solution properties of the phenyl group operating differently under the bulk conditions, used to determine the octanol-water partition coefficients, and the sterically constrained octadecysilane chain configuration, present in the C₁₈ bonded-phase HPLC column.

3.2 Application to Oil Shale

Elemental analysis of sedimentary deposits has shown the enrichment of a number of elements, including As, in the carbonaceous deposits of coal, black shale, petroleum, and asphalt over average crustal abundances [30]. Both coal and oil shale, in general, contain higher concentrations of these elements than petroleum. The increased use of coal and oil shale as alternatives to petroleum will cause the redistribution of arsenic contained in
The association of arsenic with sulfide deposits, particularly pyrite, in coal has been reported [31], although no analogous conclusions have been reported for arsenic in oil shale. The accumulation of arsenic by modern day algae may indicate the manner of enrichment of arsenic in oil shale, the fossilized remnants of ancient algal mats, by initial bioaccumulation and the subsequent metamorphosis of arsenic [32].

The partitioning of arsenic during simulated in situ oil shale retorting has shown that a significant quantity of arsenic is distributed to the product oil and the retort waters [33]. The application of the weak anion exchange separation of arsenic containing compounds to a number of retort waters generated during oil shale retorting has been performed [32], and is illustrated in Figure 6a. The chromatogram reveals the presence of arsenate, phenylarsonic acid, methanearsonic acid and a neutral arsenic-containing compound.

The origin of these organoarsenic compounds is not clear. It is possible that they are synthesized during the retorting process by the reaction of alkylhalides with arsenite, according to the Meyer reaction [34]. It is also conceivable that these organoarsenicals were initially present in the oil shale, being liberated during the retorting and partitioned into the retort waters. In order to investigate this possibility ground oil shale...
was extracted, via a Soxhlet apparatus, with methanol. Figure 6b shows the separation of arsenic containing compounds in this methanol extract, indicating the presence of a neutral arsenic containing compound, phenylarsionic acid, and arsenate. At the present time, the identification of phenylarsionic acid is only tentative because of interference from a less ionic form of arsenate found in methanolic solutions, as previously reported [29]. This less ionic form of arsenate is probably the dimethyl ester of arsenate, which has a $\Delta\phi$ value of -0.24. It is therefore predicted to elute from the column with a retention time similar to phenylarsionic acid. A recent report on the hydrolysis of arsenate triesters indicates that the first and second hydrolysis steps are very rapid, when conducted at pH ~ 12 [35]. In the present work the hydrolysis rate does not appear to be as rapid on the chromatographic time scale, possibly due to the lower pH (7.1 to 8.1) of the eluting solvent, the ammonium carbonate buffer, and the presence of the column substrate. Preliminary hydrolysis experiments of the methanol oil shale extract indicate the presence of phenylarsionic acid, but more extensive kinetic experiments and the use of an alternate measurement method are now necessary to confirm and quantitate phenylarsionic acid.

![Graph](image)

Figure 6. (A) The separation of arsenicals in a process water generated by a simulated in-situ retorting process (Lawrence Livermore National Laboratory L-2). (B) The separation of arsenicals in a methanolic extract of ground oil shale (NBS).

4. Conclusions

The correlation of the linear sum of the appropriate structural substituent parameter with the logarithm of the chromatographic capacity factor for organoarsenicals ($\phi\theta$) and tetraorganotins ($\pi$) has been found to be linear. This allows the prediction of: the
retention time of a sought after compound, the possible structure(s) of unknown compounds from experimentally determined retention times, and the possible co-elution of interfering compounds. In addition, this relationship can be used to optimize diverse chromatographic systems, including ion exchange and solvophobic mechanisms, for a desired separation. The analysis of a methanol oil shale extract has demonstrated the utility of structural substituent parameters as a diagnostic tool in the liquid chromatographic speciation of trace metals and metalloids in complex matrices commonly associated with energy-related processes.

5. Acknowledgment

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6. References


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