Solvent Extraction of Chromium by Salicylic, Thiosalicylic, and Phthalic Acids

Dennis G. Sebastian

Follow this and additional works at: https://openprairie.sdstate.edu/etd

Recommended Citation

This Thesis - Open Access is brought to you for free and open access by Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. For more information, please contact michael.biondo@sdstate.edu.
SOLVENT EXTRACTION OF CHROMIUM BY SALICYLIC, THIOSALICYLIC, AND PHTHALIC ACIDS

BY

DENNIS G. SEBASTIAN

A thesis submitted in partial fulfillment of the requirements for the degree Master of Science, Major in Chemistry South Dakota State University 1977
SOLVENT EXTRACTION OF CHROMIUM BY SALICYLIC, THIOSALICYLIC, AND PHTHALIC ACIDS

This thesis is approved as a creditable and independent investigation by the candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser Date

Head, Chemistry Department Date
ACKNOWLEDGEMENTS

I would like to express my appreciation to the following:
To Dr. David Hilderbrand for his patience and inspiration.
To my wife, Margey, for her encouragement and trust.
To my typist, Leann Mangan, for her efforts and friendship.

Dennis G. Sebastian
ABSTRACT

The use of salicylic, thiosalicylic, and phthalic acids as chelating agents for the extraction of Cr(III) from aqueous solution was investigated. Normal butanol was selected as a solvent due to its relatively low solubility in the aqueous phase. Heating of the metal-ligand mixture was necessary to accelerate complex formation. The efficiency of the extraction process was found to be dependent upon pH, heating duration, and the choice of buffer systems. The % extraction was reduced using some buffer systems due to the formation of non-extractable complexes with chromium. A potassium hydrogen phthalate buffer system was found to yield the highest % extraction. The extraction efficiency is enhanced by using NaCl as a salting-out agent. Optimum extraction conditions using the phthalate buffer are pH 3.0, 35 minutes heating, and 6.7 grams NaCl per 25 ml of aqueous phase. Under these conditions 97.3% extraction efficiency was obtained. Extraction efficiencies were calculated after analysis of samples by atomic absorption spectroscopy.

The composition of the extracted species was investigated by use of the mole ratio method and u.v.-visible spectroscopy. The ligand to metal ratio was found to be 2:1 yielding a complex of the formula Cr(L)(HL).
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>STATEMENT OF PROBLEM.</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>LITERATURE REVIEW</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>EXPERIMENTAL.</strong></td>
<td>15</td>
</tr>
<tr>
<td>Reagents</td>
<td>15</td>
</tr>
<tr>
<td>Determination of Normalized Extraction Curves</td>
<td>18</td>
</tr>
<tr>
<td>Determination of Distribution Ratios</td>
<td>20</td>
</tr>
<tr>
<td>Ashing of Samples</td>
<td>20</td>
</tr>
<tr>
<td>Analysis of Samples</td>
<td>21</td>
</tr>
<tr>
<td>Mole Ratio Experiments</td>
<td>23</td>
</tr>
<tr>
<td><strong>RESULTS AND DISCUSSION.</strong></td>
<td>24</td>
</tr>
<tr>
<td>Normalized Extraction Efficiency Curves</td>
<td>24</td>
</tr>
<tr>
<td>Salicylic Acid, Acetate Buffered</td>
<td>24</td>
</tr>
<tr>
<td>Thiosalicylic Acid, Acetate Buffered</td>
<td>26</td>
</tr>
<tr>
<td>Thiosalicylic Acid, pH Adjusted</td>
<td>26</td>
</tr>
<tr>
<td>Use of Salting Out Agents</td>
<td>29</td>
</tr>
<tr>
<td>Buffer Investigation</td>
<td>29</td>
</tr>
<tr>
<td>Phthalic Acid Extractions</td>
<td>32</td>
</tr>
<tr>
<td>Thiosalicylic Acid Extractions, KHP Buffered</td>
<td>32</td>
</tr>
<tr>
<td>Mixed Thiosalicylic-Phthalic Acid Extractions</td>
<td>35</td>
</tr>
<tr>
<td>Use of TBP As An Extraction Aid</td>
<td>37</td>
</tr>
<tr>
<td>Verification of Trends Established in Normalized Extraction Curves</td>
<td>37</td>
</tr>
<tr>
<td>Mole Ratio Experiments</td>
<td>42</td>
</tr>
<tr>
<td>Distribution Ratios</td>
<td>47</td>
</tr>
<tr>
<td><strong>CONCLUSION.</strong></td>
<td>49</td>
</tr>
<tr>
<td><strong>APPENDIX 1.</strong></td>
<td>50</td>
</tr>
<tr>
<td><strong>APPENDIX 2.</strong></td>
<td>51</td>
</tr>
<tr>
<td><strong>APPENDIX 3.</strong></td>
<td>52</td>
</tr>
<tr>
<td><strong>APPENDIX 4.</strong></td>
<td>54</td>
</tr>
<tr>
<td><strong>FOOTNOTES</strong></td>
<td>55</td>
</tr>
<tr>
<td><strong>BIBLIOGRAPHY.</strong></td>
<td>59</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. IONIZATION CONSTANTS OF ACIDS USED</td>
<td>10</td>
</tr>
<tr>
<td>II. BUFFER EFFECTS</td>
<td>31</td>
</tr>
<tr>
<td>III. EFFECT OF HEATING DURATION ON %E</td>
<td>38</td>
</tr>
<tr>
<td>IV. EFFECT OF SALT CONCENTRATION ON %E</td>
<td>40</td>
</tr>
<tr>
<td>V. EFFECT OF PH ON %E</td>
<td>41</td>
</tr>
<tr>
<td>VI. OBSERVED PERCENT EXTRACTION VALUES</td>
<td>48</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. STRUCTURES OF LIGAND ACIDS</td>
<td>2</td>
</tr>
<tr>
<td>II. SPLITTING OF d ORBITALS IN AN OCTAHEDRAL FIELD</td>
<td>6</td>
</tr>
<tr>
<td>III. OTHER CHELATING AGENTS USED IN CHROMIUM EXTRACTION</td>
<td>8</td>
</tr>
<tr>
<td>IV. ATOMIC ABSORPTION CALIBRATION CURVE</td>
<td>22</td>
</tr>
<tr>
<td>V. SALICYLIC ACID WITH ACETATE BUFFER</td>
<td>25</td>
</tr>
<tr>
<td>VI. THIOSALICYLIC ACID WITH ACETATE BUFFER</td>
<td>27</td>
</tr>
<tr>
<td>VII. THIOSALICYLIC ACID - pH ADJUSTED</td>
<td>28</td>
</tr>
<tr>
<td>VIII. PHTHALIC ACID WITH KHP BUFFER</td>
<td>33</td>
</tr>
<tr>
<td>IX. THIOSALICYLIC ACID WITH KHP BUFFER</td>
<td>34</td>
</tr>
<tr>
<td>X. THIOSALICYLIC WITH PHTHALIC ACID KHP BUFFER</td>
<td>36</td>
</tr>
<tr>
<td>XI. MOLE RATIO PLOT THIOSALICYLIC ACID</td>
<td>44</td>
</tr>
<tr>
<td>XII. MOLE RATIO PLOT PHTHALIC ACID</td>
<td>45</td>
</tr>
<tr>
<td>XIII. MOLE RATIO PLOT THIOSALICYLIC ACID VARIABLE PHTHALIC ACID 1-1 MOLE RATIO</td>
<td>46</td>
</tr>
</tbody>
</table>
STATEMENT OF THE PROBLEM

The purpose of this research was to investigate the utility of salicylic, thiosalicylic, and phthalic acids (Figure I) as complexing agents in the solvent extraction of chromium. These studies were performed with the goal of selecting a complexing agent and extraction conditions which would enable chromium to be extracted reproducibly and quantitatively. While this research in itself represents only a first step, the ultimate goal would be a system for use in routine determination of chromium at low concentrations. The need for such a system is evident from the fact that the Association of Official Analytical Chemists has not as yet published an official method of chromium analysis in biological samples.¹ Extraction techniques yield two advantageous effects. First, extraction of metal ions results in a simpler matrix for the analyte, which reduces interference effects. Second, an efficient extraction process may result in chemical enrichment, making analysis more accurate for species at low concentration.

Such analyses are important in light of increasing interest in dietary and environmental chromium concentration. Dietary deficiencies of chromium have been linked to symptoms resembling diabetes in humans. The chromium concentrations in a sampling of major food classes vary from a low of 0.03 ppm in meats to a high of 3.62 ppm in vegetables.² Environmental studies of chromium in
Salicylic Acid

\[
\begin{align*}
\text{Salicylic Acid} & \quad \begin{array}{c}
\text{\includegraphics[width=0.3\textwidth]{salicylic_acid.png}}
\end{array}
\end{align*}
\]

Thiosalicylic Acid

\[
\begin{align*}
\text{Thiosalicylic Acid} & \quad \begin{array}{c}
\text{\includegraphics[width=0.3\textwidth]{thiosalicylic_acid.png}}
\end{array}
\end{align*}
\]

O-Phthalic Acid

\[
\begin{align*}
\text{O-Phthalic Acid} & \quad \begin{array}{c}
\text{\includegraphics[width=0.3\textwidth]{ophthalic_acid.png}}
\end{array}
\end{align*}
\]

Figure I
connection with heavy metals pollution from coal and petroleum are also important. These materials contain 5-20 ppm and 0.0015-0.0018 ppm chromium respectively. Chromium in urban air was placed as high as 0.1 ug/m^3 in 1967. O.S.H.A. has reported that chromium intake of 400 mg/kg of body weight causes cancer in white rats, so increased use of coal in the future will warrant monitoring of atmospheric chromium content.

The extraction-enrichment phase of such analyses is important in view of the low chromium levels compared to detection limits of analytical methods and potential matrix interference effects. Prior to analysis the chromium must frequently be extracted from ashed residues of materials such as sewage sludge, coal, biological samples, or acid washings of air sampling filters. These samples are of variable composition and chromium analysis in situ could result in poor reproducibility of analytical data due to inconsistent desolvation and background absorption in atomic absorption analysis.
While many metals yield high percent extraction (E) values with a variety of chelating or complexing agents, there are few extraction systems reported which approach 100% E for a one step extraction of chromium. The inefficiency of most chromium extraction systems is due to the inertness of the hexaquochromium ion \( \text{Cr(H}_2\text{O)}\text{)}_6^{+3} \). The lability of this species has been studied by isotopic methods employing water molecules labeled with \( ^{18}O \). The half-life of the hexaquochromium species has been reported as approximately 40 hours in a one molar solution of chromium(III).\(^6\) The rate constant for the reaction

\[
\text{Cr(H}_2\text{O)}\text{)}_6^{+3} + \text{H}_2\text{O}^* \rightarrow \text{Cr(H}_2\text{O)}_5\text{H}_2\text{O}^* + \text{H}_2\text{O}
\]

has been assigned values ranging from \( 2 \times 10^{-5} \) sec\(^{-1} \) to \( 4.8 \times 10^{-6} \) sec\(^{-1} \).\(^8\) These values can be compared to those of the more readily substituted Copper(II) ion at \( 2 \times 10^{8} \) sec\(^{-1} \), Iron(II) at \( 3 \times 10^{6} \) sec\(^{-1} \), and Iron(III) at \( 2.5 \times 10^{2} \) sec\(^{-1} \).\(^9\)

Aquation and other substitutions of octahedrally coordinated cations are generally presented as SN\(_1\) or unimolecular mechanisms. A traditional SN\(_1\) mechanism would imply spontaneous expulsion of a coordinated water molecule prior to appreciable interaction with the entering group; however, varying ionic strengths and different types of salts have been shown to alter the rate of substitution by ligands in \( \text{Cr(H}_2\text{O)}\text{)}_6^{+3} \). This effect has been attributed to dipole interactions.
with the coordinated water molecules and to lowered stability of partially formed complexes, for example CrF$_2$(H$_2$O)$_4^{+1}$. The substitution mechanism is therefore not a pure unimolecular dissociation since it can be affected by the presence of other species.

The inertness of the hexaquochromium ion has been explained, in valence bond terminology, by the substitution properties of the filled d orbital system as shown below.

The filled d system does not permit use of the more stable low-lying d orbitals in forming the seven-membered transition state of an SN$_2$ type substitution, therefore the d orbitals of a higher principal quantum number must be used. As a result the activation energy for the reaction is higher than it would be if the low-lying d orbitals were available. The stability of the d$^2$sp$^3$ hybrid orbitals in the complex also inhibits the shift to a five-membered transition state assumed in an SN$_1$ type mechanism. This explanation, however, offers no interpretation of the inertness of the Cr(H$_2$O)$_6^{+3}$ ion relative to other d$^2$sp$^3$ systems.

The Crystal Field Theory (CFT) offers an explanation for this phenomenon and has generally supplanted the valence bond theory in describing octahedral complexes of transition metals. The CFT
pictures a splitting of the five d orbitals into higher and lower energy states in an octahedral field. Those orbitals along the axes pointing toward the ligands assume energies higher than in the uncomplexed state and those orbitals away from the ligands assume lower energy states. The splitting of the d orbitals of the chromium(III) ion is represented in Figure II.

\[ \Delta = x^2 - y^2 = z^2 \]

The energy difference between these two states is the crystal field splitting energy \( (\Delta) \). Chromium(III) is a \( d^3 \) ion and its 3 d electrons are distributed unpaired in the lower-energy orbital set. The energy difference between the uncomplexed and complexed state can be significant and is referred to as the crystal field stabilization energy. This stabilization energy must be overcome if the system is to change to either the 5 or 7 coordinate transition states involved with SN\(_1\) or SN\(_2\) substitution mechanisms and therefore adds to the activation energy of the transition state.\(^{15}\) Ions with a \( d^3 \) or \( d^6 \) configuration would be expected to exhibit this inertial effect and in fact the substitution rates of cobalt(III), a \( d^6 \)
ion, are even lower than those of chromium(III). The Crystal Field Theory has itself been supplanted by the ligand field and molecular orbital pictures of transition metal complexes, but the concept of d orbital splitting in these theories is substantially the same as in the CFT.

Chromium(III) was chosen for extraction because it is a stable oxidation state and is capable of forming complexes. In comparison, Chromium(II) is easily oxidized by atmospheric oxygen to chromium(III) and chromium(VI) is already "complexed" in aqueous solution as the chromate or dichromate ion. Among the reported chromium(III) extraction methods are those employing acetylacetone, thenoyltrifluoroacetone, hydroxyquinoline, diethyldithiocarbamate, and 1-phenyl-3-methyl-4-benzoylpyrazolone-5- (PMBP). The structures of these compounds are given in Figure III. Extractions using these reagents share a common difficulty of yielding low extraction efficiencies at room temperature. The formation of an extractable complex is increased by heating the solutions and the extraction approaches 100 percent at elevated temperatures (80-100°C). Flett and Jaycock have reviewed the use of carboxylic acids in metal ion extraction and report that Russian workers have used C7-C9 fatty acids and naphthenic acids in the extraction of chromium(III), but no values of extraction efficiency are given. Extraction of chromium(III) by heptafluorobutyric acid has been reported, but no details as to the efficiency were given.

While Aggett and co-workers have studied the extraction of
**Figure III**

**OTHER CHELATING AGENTS USED IN CHROMIUM EXTRACTION**
trivalent metal ions such as aluminum(III) and iron(III) with salicylic acid, no reported work on the extraction of chromium(III) by this reagent was found. Since a distribution ratio of 7.94, yielding a possible 88% extraction of iron(III) was reported, salicylic acid was deemed worthy of investigation in the case of chromium extraction. The related sulfur derivative of salicylic acid, thiosalicylic acid, was also investigated in the belief that the greater dissociation of the sulfhydryl group would enhance the chelation of the metal ion by furnishing a larger percentage of doubly ionized species at a given pH than present with salicylic acid. The acid dissociation constants were shown in Table I. It was also felt that the lower electronegativity of the sulfur atom would enhance the stability of the species formed, as donor atoms of lower electronegativity generally lead to improved complex stability by forming more covalent bonds. The third complexing agent investigated, phthalic acid, had been studied by Lumme and Tummavouori as a precipitating agent for chromium(III), forming polymeric precipitates in the presence of high hydroxide concentrations (2 M). As in the case of thiosalicylic acid, phthalic acid offers the advantage of a higher second ionization constant than salicylic acid.

One can obtain a qualitative picture of the effect of acid dissociation constants ($K_a$), complex formation constants ($\beta$), and ligand ($K_{d,a}$) and complex ($K_{d,c}$) distribution coefficients on the degree of metal extraction by examining the $K_{ex}$ or extraction
Table I

IONIZATION CONSTANTS OF ACIDS USED

<table>
<thead>
<tr>
<th>Acid</th>
<th>Ka at (\text{l}_{\text{H}})</th>
</tr>
</thead>
</table>
| Salicylic\textsuperscript{23} | \(K_1: 1.3 \times 10^{-3}\)  \\
|                 | \(K_2: 8 \times 10^{-14}\)  |
| Phthalic\textsuperscript{23}  | \(K_1: 1.6 \times 10^{-3}\)  \\
|                 | \(K_2: 8 \times 10^{-6}\)   |
| Thiosalicylic\textsuperscript{24} | \(K_1: 1.3 \times 10^{-3}\) (assumed)  \\
|                 | \(K_2: 1.32 \times 10^{-9}\) |
constant for the following reaction.

$$M^{n+} + n(\text{HL})_{\text{org}} \rightleftharpoons (\text{MLn})_{\text{org}} + n\text{H}^+$$

$$K_{\text{ex}} = \frac{[\text{MLn}]_{\text{org}}[\text{H}^+]_{\text{aq}}}{[M^{n+}]_{\text{aq}}[\text{HL}]_{\text{org}}^n}$$  \hspace{1cm} \text{equation I}$$

$K_{\text{ex}}$ is given in equation I which reduces to

$$K_{\text{ex}} = \left(\frac{K_a}{K_{D,1}}\right)^n K_{D,c} \beta$$  \hspace{1cm} \text{equation II}$$

as detailed in Appendix 2.\textsuperscript{27} The terms involved are defined in Appendix 1. One can readily observe that a higher formation constant yields a higher $K_{\text{ex}}$ and therefore a larger concentration of \((\text{MLn})_{\text{org}}\), the extracted species. Since the complexing ability tends to increase as the basicity of the ligand, one would assume that the more basic the ligand the greater the $\beta$ obtainable with a given metal ion.\textsuperscript{28} However, the extent of complex formation depends not only on the stability of the product, but also on the amount of dissociated ligand present. Thus a compromise is necessary between the basicity of the ligand and the ligand dissociation. This is seen in equation II, as $K_{\text{ex}}$ varies directly with both the dissociation constant of the acid and the formation constant. $K_{\text{ex}}$ is also inversely proportional to the $K_D$ of the ligand acid and is, as expected, directly proportional to the $K_D$ of the complex.

Selection of a buffer system for this study represented a
problem in that some common buffer ions form stable complexes with chromium(III), which inhibited extraction. Inhibition occurred either through observable precipitation or formation of complexes presumably more soluble in water than in the organic layer. A series of buffers was studied in attempts to overcome this problem.

A recognized method of improving the efficiency of solvent extraction processes is the use of salting out agents. Although this technique is usually applied in ion-pair formation systems rather than complex or chelate systems, it has potential benefits in all extraction systems. Salting agents are added to the system prior to separation of the organic and aqueous phases. Salt concentrations should be near the saturation point, but low enough to insure ease of solution and avoid the problem of adsorption of the complex onto any undissolved portion. The addition of salt in levels approaching the saturation point has a three-fold effect on the distribution ratio. As the saturation point is reached, an increasing number of $H_2O$ molecules become fixed in the hydrated sheaths of the added ions, causing fewer free water molecules to be available for interaction with the complex. The organic portions of the complex will exhibit lowered solubility in the salted systems as solutions of concentrated electrolytes increase the activity coefficients of non-polar species. Large concentrations of electrolytes also lower the dielectric constant of a polar solvent, thus increasing the tendency toward complete
formation of the complex. This would not be important in the case of a conventional chelate extraction where bonding is through both an unshared pair of ligand electrons and an ionized coordination site in the same molecule. A neutral species with three equivalently bonded ligands would be formed with a trivalent ion in this conventional case. The complete formation of the chelate, once the inertness of the hexaquochromium ion had been overcome, would be thermodynamically favored due to the chelate effect or the entropy effect of replacing 6 H₂O molecules with 3 molecules of ligand. In the extraction systems studied only one molecule of carboxylic acid is chelated to the central ion while the second molecule functions as a monodentate ligand. The ability of high salt concentrations to reduce the dielectric constant may enhance the pairing of the chelated metal ion and the second ligand anion.

An additional method of enhancing extraction efficiencies is addition of neutral species that can replace H₂O in the coordination sites not filled by the complexing ligand. The species used consist of a polar group with unshared electron pairs incorporated into a molecule with organic groups of low polarity. While the molecule is capable of interacting with cations through the polar group, the organic groups cause the resulting complex to be less water soluble. An example of such a species is tri-n-butyl phosphate (TBP) which coordinates to the cation through an oxygen of the phosphate group. TBP is a liquid and can therefore be used as the only organic solvent or can be mixed with other organic solvents in an extraction.
system.

The ratio of ligand to acid in the extracted species was also investigated. The major ionized ligand species in solution at pH values low enough to prevent precipitation of Cr(OH)$_3$ is HL$^-$ as calculated from dissociation constants in Appendix 3. Thus extraction of complex of the formula Cr(HL)$_3$ might occur. Chelation of the metal ion can also occur. However, as already noted, this requires coordination of electron pairs from two ionized sites per chelated ligand molecule. A neutral extractable species would therefore be of the form Cr(L)(HL). Aggett and co-workers have reported species of the second type for extraction of trivalent aluminum and iron with salicylic acid.\textsuperscript{35} Khadikar and Kakkar have isolated and determined percent composition of chromium complexes with salicylic acid and thiosalicylic acid which gave the respective formulas Cr(C$_7$H$_4$O$_3$)$_2$Na•2H$_2$O, Cr(C$_2$H$_4$O$_2$S)$_2$Na•2H$_2$O.\textsuperscript{36} Mole ratio determinations can be used to investigate the ligand to metal ratio existing in solution.
EXPERIMENTAL

The instrumentation and procedures used in the investigation are described in the following section. Reagents selected or prepared according to specific requirements are discussed. All other reagents were selected on the basis of required quality for their particular use.

CHROMIUM SOURCE

Chromium(III) chloride hexahydrate; Matheson, Coleman, and Bell Reagent grade, was used as the source of chromium for extraction. The structure of the compound is believed to be \( \text{Cr(H}_2\text{O)}_4\text{Cl}_2 \cdot \text{Cl} \cdot \text{2H}_2\text{O} \). The compound melted at approximately 80° C during attempts at oven drying. Drying was omitted in the determination of the normalized extraction curves. The need for removal of surface moisture was tested by placing the compound in a dessicator containing 70-80 ml concentrated sulfuric acid. The compound will lose 2 moles of \( \text{H}_2\text{O} \) in extended contact with \( \text{H}_2\text{SO}_4 \), but in this case the weight loss was negligible (0.17%). The stock solution was standardized by analysis against the chromium standard solution described below. The nominal chromium concentration of stock solution was 520 ppm.

CHROMIUM CALIBRATION STANDARD

Potassium dichromate (\( \text{K}_2\text{Cr}_2\text{O}_7 \)); Fisher Scientific Company Analytical Reagent grade, was used in establishing the standard curve for atomic absorption analysis. This reagent was oven dried overnight prior to preparation of a stock dichromate solution.
containing 1000 ppm chromium.

**SALICYLIC ACID**

Salicylic acid; Mallinckrodt Reagent Grade, was used; 2.06 grams was dissolved in n-butanol and taken to volume in a 100 ml volumetric flask to give a 0.15 molar solution for use in extraction.

**THIOSALICYLIC ACID**

Thiosalicylic acid; Eastman Organic Chemicals practical grade, was used as provided; 2.31 grams was taken to prepare 100 ml of 0.15 molar solution as detailed above.

**PHTHALIC ACID**

Phthalic acid; Eastman Organic Chemicals practical grade, was used as provided. Phthalic acid was used at 0.1 M concentration since it did not dissolve in n-butanol as readily as the other acids. Solutions were prepared by dissolving 1.66 grams in 100 ml of n-butanol.

**MIXED EXTRACTION SOLUTION**

Solutions which were both 0.15 M in thiosalicylic acid and 0.1 M in phthalic acid were also prepared.

**BUFFER SYSTEMS**

Acetate buffers were prepared from reagent grade sodium acetate and acetic acid. The correct ratios for a given pH were determined by the Henderson-Hasselbalch equation.

\[ \text{pH} = pK_a + \log \left( \frac{[\text{salt}]}{[\text{acid}]} \right) \]
The combined molarity of acetate and acid was 0.1 molar.

Phosphate buffers were prepared as above.

Nitrite buffers were prepared from reagent grade NaNO$_2$ and HCl. A 0.1 molar solution of NaNO$_2$ was prepared from the salt. The concentration of HNO$_2$ for a given pH was calculated and a quantity of 0.1 N HCl was added to the nitrite solution to generate the derived concentration of HNO$_2$. This procedure was necessary due to the instability of HNO$_2$. 38

Potassium acid phthalate (KHP) buffers were prepared from 0.1 M solutions of KHP and either 0.1 N HCl or 0.1 N NaOH depending on the pH required. Fifty ml of the KHP were mixed with volumes of acid or base selected from the table below. 39

<table>
<thead>
<tr>
<th>pH</th>
<th>Vol. of 0.1 M HCl (ml)</th>
<th>Vol. of 0.1 M NaOH (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>38.8</td>
<td></td>
</tr>
<tr>
<td>3.00</td>
<td>22.3</td>
<td></td>
</tr>
<tr>
<td>3.50</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>4.50</td>
<td></td>
<td>8.7</td>
</tr>
</tbody>
</table>

**1-BUTANOL**

The solvent chosen for use as the extraction solvent was 1-butanol. The density of the alcohol is 0.81 g/ml, making the organic layer the upper layer when carrying out an extraction. The solubility is 7.9 g/100 ml of water at 20° C which represents a volume increase of 9.8 ml/100 ml H$_2$O assuming additive volumes.
DETERMINATION OF NORMALIZED EXTRACTION CURVES

The source of chromium for extraction was a 0.01 M solution (520 ppm chromium) prepared from CrCl₃. The stock solution was made mildly acid (approximately pH 3.5) to prevent chromium loss by precipitation as hydroxides. A 40 ml aliquot of this solution was adjusted to the desired pH by addition of 0.1 N NaOH and 0.1 N HCl. The pH values were obtained using a Sargent-Welch model LS pH meter calibrated with a pH 4 or pH 7 standard buffer depending on the pH range to be determined. This solution was then quantitatively transferred to a 100 ml volumetric flask and taken to volume using a buffer solution of the desired pH. A 10 ml aliquot of the resulting solution was used for extraction. At this point the chromium concentration was 0.004 molar. A 10 ml aliquot of the organic acid dissolved in 1-butanol was added. Since ligand concentrations vary from 0.1 to 0.25 molar, the minimum concentration ratio of ligand to metal is 25:1. The resulting mixture was refluxed in a 100 ml round bottom flask for 30 minutes. Reflux temperatures were approximately 91° C. The samples were allowed to cool to ambient temperature before separation of the layers. The round bottom flask was washed with equal portions (5 ml) of 1-butanol and distilled H₂O and the washings were added to the bulk of the mixture held in a separatory funnel. If no salt was to be added the layers were separated at this point. If salt was added the funnel was capped and shaken until the salt dissolved. The organic layer was transferred quantitatively with a butanol rinse to a 50 ml volumetric flask, taken to volume
with butanol and shaken to insure homogeneity. A 10 ml aliquot of this solution was taken for analysis. The organic matter was destroyed by wet oxidation. The aqueous solution resulting from the ashing process was quantitatively transferred to a 25 ml volumetric flask. The samples were then analyzed by atomic absorption spectrophotometry. Extraction efficiencies were determined by calculating theoretical chromium recovery assuming 100% extraction and comparing experimental values to this figure as shown below:

\[
520 \text{ ppm (stock solution)} \times \frac{40}{100} \times \frac{10}{50} \times \frac{10}{25} = 16.6 \text{ ppm}
\]

\[
\%E = \frac{\text{final experimental concentration}}{16.6 \text{ ppm}} \times 100
\]

Extractions were run at 0.5 pH unit intervals from pH 2.5-4.5 or until a definite maximum in the curve was established.

A more convenient method of solution preparation was used in the final series of extractions. This method eliminated the need for preparing a fresh 208 ppm chromium stock solution at each pH value under investigation. A 40 ml aliquot of 520 ppm solution was diluted to 100 ml using distilled water adjusted to pH 3.5 with dilute (0.1 N) HCl. For extraction purposes a 10 ml aliquot of this solution was mixed with 10 ml of the correct buffer. The ligand acids were then added to the mixture, 10 ml of each for a combined system or 10 ml acid solution and 10 ml butanol if only one extractant was to be used. Thus the total amounts of ligand and metal ion were the same as in the previous method although their
concentrations in the respective layers were halved.

**DETERMINATION OF DISTRIBUTION RATIOS**

Distribution ratios were determined by separation and analysis of the complete aqueous and organic layers. Each layer was transferred to a 50 ml volumetric flask and weighed on an analytical balance. The original volume of solution was determined by the following procedure. The flasks were filled to volume with the respective solvent and reweighed. The volume of solvent added was then determined by density calculations. A 10 ml aliquot of each sample was taken for analysis. This method permitted calculation of extraction efficiency, distribution ratio, and chromium recovery from one set of analyses.

**ASHING OF SAMPLES**

All extraction samples were ashed by wet oxidation using nitric, perchloric, and sulfuric acid mixtures. Ashing was performed in a Kjeldahl rack using 100 ml Kjeldahl flasks. The Kjeldahl rack exhausts the fumes through a water aspirator and thus prevents release of acid fumes to the hood vent. This avoids the buildup of explosive perchlorates in the hood exhaust system. Preliminary oxidation was performed with 10 ml of 50/50 concentrated HNO₃/H₂O mixture. The samples were boiled until a considerable reduction in volume occurred. At this point, all of the water insoluble organics were removed and all readily oxidized water soluble organic material is digested. The samples were cooled and 5 ml of a 5:1:1 solution of
concentrated HNO₃, 72% HClO₄, and concentrated H₂SO₄ was added. The samples were heated until fumes of perchloric acid appeared.

**ANALYSIS OF SAMPLES**

The ashed samples were quantitatively transferred to 25 ml volumetric flasks and taken to volume with distilled water. Solutions of 0, 10, 30, and 50 ppm chromium were prepared using the dichromate stock solution. One ml of both HClO₄ and H₂SO₄ was added to each standard in order to match the matrix of the samples. In determination of the normalized extraction curves the samples and standards were not reduced to the same oxidation state. In subsequent analyses one ml of 0.5 M Na₂SO₃ was added to both samples and standards, reducing chromium(VI) to chromium(III). (See Appendix 4). The analyses were performed on a Perkin Elmer model 303 atomic absorption spectrophotometer using a premix burner with an air-acetylene flame. This oxidizer-fuel combination provides a flame temperature of approximately 2200°C. The flame was made slightly fuel rich to prevent formation of refractory oxides of chromium. A Perkin Elmer signal averaging unit was used to determine absorbance. Average values from four individual absorbance readings were determined for each sample.

The concentrations were determined by use of a calibration curve run with each set of samples. A typical calibration curve is seen in Figure IV.
FIGURE IV
ATOMIC ABSORPTION CALIBRATION CURVE

Absorbance at 358 nm

ppm chromium
MOLE RATIO EXPERIMENTS

The mole ratio method for determining the number of ligands involved in complex formation was used. Solutions which were 0.01 molar in both chromium(III) and ligand were prepared in 50/50 alcohol/H₂O solvent. The solutions were mixed with varying ratios of ligand to a fixed concentration of chromium. The solutions were then heated to 85-90°C for 15 minutes and allowed to cool to ambient temperature before dilution and spectra determination. U.V.-visible spectra for the unmixed and mixed reagents were obtained.
RESULTS AND DISCUSSION

The results of the experimental procedures described above are presented in this section. The variation of the extraction efficiency with pH and the relative efficiencies of the three ligands are presented as normalized extraction curves. The results of the investigation of buffer properties, salt effects, heating duration, and distribution ratios are also presented.

NORMALIZED EXTRACTION EFFICIENCY CURVES

The normalized extraction efficiency curves represent the results of experiments run to evaluate the effect of pH on the extraction efficiency of various combinations of acids and buffers. The curves are presented in Figures V thru X. These analyses indicate the optimum pH range of extraction and provide a means of comparison of extraction systems. The extraction efficiencies were normalized against the thiosalicylic-phthalic acid system which gave the highest extraction efficiency (approximately 100%). The extraction efficiency at the pH of maximum extraction for the thiosalicylic-phthalic acid system was assigned a value of unity. The extraction efficiencies of other systems are reported as fractions of the efficiency obtained with the thiosalicylic-phthalic acid system.

SALICYLIC ACID, ACETATE BUFFERED

The results of the extraction of chromium with salicylic acid are presented in Figure V. The extraction was studied in the pH
FIGURE V
SALICYLIC ACID WITH ACETATE BUFFER

Normalized Extraction Efficiency

pH

3.0 3.5 4.0 4.5 5.0
range 3.5-5.0. A maximum in the extraction curve occurs at pH 4.5 yielding a normalized extraction efficiency of 0.41. Ordinarily chromium(III) begins to precipitate as Cr(OH)$_3$ in this pH region, but the stability of the acetate complex prevents precipitation in solutions of higher hydroxide concentration. Salt was not used as an extraction aid in determining these results.

**THIOSALICYLIC ACID, ACETATE BUFFERED**

The results of the thiosalicylic acid, acetate buffered extractions are presented in Figure VI. The extraction curve for this system shows improved extraction efficiency at a lower pH than the salicylic acid extraction, yielding a normalized extraction efficiency of 0.55. This could be attributed to a higher formation constant of the complex due to the lower electronegativity of sulfur as the second donor in the chelate and to the higher dissociation of the sulfhydryl group compared to that of the hydroxyl. Calculations presented in appendix 3 show that the thiosalicylic acid provides approximately $1.65 \times 10^4$ times as much doubly ionized species as the salicylic acid at pH 3.5. Salt was not used as an extraction aid.

**THIOSALICYLIC ACID, pH ADJUSTED**

The results of the pH adjusted thiosalicylic acid extractions are presented in Figure VII. Extractions were performed on unbuffered thiosalicylic acid systems to ascertain if the low extraction efficiencies obtained in the previous analyses were the
FIGURE VI
THIOSALICYLIC ACID WITH ACETATE BUFFER

Normalized Extraction Efficiency

pH
FIGURE VII
THIOSALICYLIC ACID - pH ADJUSTED

Normalized Extraction Efficiency

SALT

NO SALT

pH

Normalized Extraction Efficiency
result of competitive formation of a non-extractable acetate complex.
The pH values in the figure represent initial pH, attained by adjustment with 0.1 N HCl or 0.1 N NaOH. The lack of buffering allowed the pH to drop as the ligand acid ionized, inhibiting further ionization, particularly when the initial pH values were low. Extraction efficiency increased at higher pH to values greater than those achieved with acetate systems, the maximum being 64% of the standard value. The extraction efficiency decreases above pH 4.5, apparently due to the formation of insoluble hydroxides. The comparison of these results with those of the acetate buffered extractions indicates that acetate ion may interfere with the extraction.

USE OF SALTING OUT AGENTS

Figure VII also includes results of extractions in which 3 grams of NaCl were added to the separatory funnel prior to separation of the layers. The addition of NaCl aids in extraction of the thiosalicylic acid-chromium complex yielding a 13% absolute improvement in extraction efficiency.

BUFFER INVESTIGATION

Acetate ion as indicated by the results of Figures VI and VII and as reported by Berg, forms highly stable complexes with chromium. These complexes were not extractable under the conditions present in these experimental procedures. The pH adjusted extractions with thiosalicylic acid indicated the necessity of a buffering system, so
several possible buffer systems were investigated. The characteristics of the various buffer systems are summarized in Table II.

The phosphate buffer, when refluxed with the chromium(III) solution formed a light green precipitate. The composition of this precipitate was not investigated and the use of phosphate buffers was not pursued further.

The nitrite buffer yielded no adverse results on refluxing with chromium(III) solution. However, when used in conjunction with an actual extraction a lightly colored insoluble residue was formed. Since no apparent precipitation occurred in reflux with the chromium solution, it appeared that reaction with the thiosalicylic acid must have taken place. Use of the nitrite buffer with salicylic acid caused a reddish brown extractable complex to form. No precipitation was noted. It is possible that nitrosation of the salicylic acid occurred. Further investigation of the nitrite buffer systems was not pursued.

Potassium acid phthalate (KHP) buffered extractions were investigated next. Lumme had utilized potassium acid phthalate in a qualitative analysis scheme and reported that solutions of chromium(III) were stable to precipitation in the presence of KHP. However, formation of precipitate was observed when KHP buffered solutions were allowed to stand for several hours. KHP buffers were used in extractions and yielded considerable improvement in extraction efficiencies. The improvement may be due simply to the elimination of the acetate complex, the formation of a secondary
<table>
<thead>
<tr>
<th>Acetate</th>
<th>Competitive Complex Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate</td>
<td>Precipitate Forms</td>
</tr>
<tr>
<td>Nitrite</td>
<td>Precipitate With Thiosalicylic Acid</td>
</tr>
<tr>
<td></td>
<td>Nitrosation (?) With Salicylic Acid</td>
</tr>
<tr>
<td>KHP</td>
<td>Competitive Extractable Complex?</td>
</tr>
<tr>
<td></td>
<td>Mixed Complex or Chelate?</td>
</tr>
</tbody>
</table>
extractable complex, or to the formation of a mixed extractable complex. Extractions using KHP buffer and a combination of the buffer and a solution of phthalic acid in butanol as the sole complexing agent were run to investigate the extraction capabilities of the phthalate anion.

**PHTHALIC ACID EXTRACTIONS**

Phthalic acid extractions were run using the KHP buffer for pH control. The results are presented in Figure VIII. These extractions were run only in conjunction with the salting-out technique. Phthalic acid exhibits a strong ability to extract chromium, yielding extraction efficiencies that were 99% of these achieved with the normalization standard. These results prompted the investigation of the extraction properties of mixed thiosalicylic-phthalic acid systems in addition to those of KHP buffered thiosalicylic acid.

**THIOSALICYLIC ACID EXTRACTIONS, KHP BUFFERED**

The results of the thiosalicylic acid-KHP buffered extractions are presented in Figure IX. The salted-out extraction with thiosalicylic acid gives considerably higher extraction efficiencies than the unsalted system. The system yields extraction efficiencies slightly lower than those with phthalic acid, and the pH range of efficient extraction is more limited. The region of maximum efficiency is centered around pH 3.5.
FIGURE VIII
PHTHALIC ACID WITH KHP BUFFER

Normalized Extraction Efficiency

SALT

pH

0.50

0.60

0.70

0.80

0.90

1.00

2.0

2.5

3.0

3.5

4.0

4.5

5.0
FIGURE IX
THIOSALICYLIC ACID WITH KHP BUFFER

Normalized Extraction Efficiency

SALT

NO SALT

pH
2.0 2.5 3.0 3.5 4.0 4.5

0.50 0.60 0.70 0.80 0.90 1.00
MIXED THIOSALICYLIC-PHTHALIC ACID EXTRactions

The results of the thiosalicylic-phthalic acid extractions are presented in Figure X. The salted extraction with the mixed system exhibits a broadened pH range of high extraction efficiency as compared to thiosalicylic acid alone. This broadening may be due to the presence of the phthalic acid as the curve follows the same general shape as the phthalic acid extraction curve. The colors of the solution in the organic and aqueous layers indicate that thiosalicylic acid or a mixed complex must be involved in extracting the chromium since green solutions are formed with the mixed system, the same as when thiosalicylic acid is used as the sole ligand. The complex formed when phthalic acid alone is used is light blue. It seems possible that thiosalicylic acid would assume the chelated position since it would form a six-membered ring which should exhibit less deviation from the normal covalent bond angles than the seven-membered ring necessary with phthalic acid. The formula $\beta = \left(\frac{n-2}{n}\right) 180^\circ$ can be used to calculate the interior angle of a regular polygon, $45^\circ$ is the interior angle and $n$ is the number of sides. For a six-membered ring this gives an angle of $120^\circ$ and an angle of $128.5^\circ$ for a seven-membered ring. The normal bond angle for sp$^3$ hybridized atoms is $109^\circ$ while that of sp$^2$ species is $120^\circ$, so the seven-membered ring would be more strained and less stable than a six-membered ring. The nature of the extracted species will be further discussed in the section on the mole-ratio experiments.
FIGURE X
THIOSALICYLIC WITH PHTHALIC ACID
KHP BUFFER

Normalized Extraction Efficiency

SALT

NO SALT

pH
USE OF TBP AS AN EXTRACTION AID

The use of tri-n-butyl phosphate as an extraction aid was not successful in these extractions. Mixtures of ligand solutions with 1 part TBP to 9 parts butanol yielded no greater extraction efficiency than solutions using only butanol as the solvent. When the ligands were dissolved in pure TBP the layers were difficult to separate and once separated the TBP layer was difficult to ash completely. No successful analyses of the organic layers were obtained, although distribution of the colored complex indicated that extraction was taking place.

VERIFICATION OF TRENDS ESTABLISHED IN NORMALIZED EXTRACTION CURVES

The relative effectiveness of the extraction systems was verified by further experimentation. A more convenient preparation of the chromium solution was used as discussed in the experimental section. Samples of the 208 ppm chromium solution used for a series of extractions were analyzed at the same time as the samples resulting from the experimental work. This method of analysis compensates for day to day instrumental variation or inconsistency in calibration standards.

The new method of solution preparation resulted in a total of 40 ml of solution during the heating step. This difference in volume from previous extractions led to reevaluation of heating duration necessary for optimum percent extraction. Table III compares the effect of heating duration for extractions run under the same conditions of pH and salt concentrations. The duration
Table III

EFFECT OF HEATING DURATION ON %E

<table>
<thead>
<tr>
<th>pH</th>
<th>Total NaCl (g)</th>
<th>Time (min.)</th>
<th>%E</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>5.8</td>
<td>20</td>
<td>92.0</td>
</tr>
<tr>
<td>3.0</td>
<td>5.8</td>
<td>25</td>
<td>93.3</td>
</tr>
<tr>
<td>3.0</td>
<td>5.8</td>
<td>30</td>
<td>94.7</td>
</tr>
<tr>
<td>3.0</td>
<td>6.7</td>
<td>20</td>
<td>90.4</td>
</tr>
<tr>
<td>3.0</td>
<td>6.7</td>
<td>25</td>
<td>93.8</td>
</tr>
<tr>
<td>3.0</td>
<td>6.7</td>
<td>30</td>
<td>96.5</td>
</tr>
<tr>
<td>3.0</td>
<td>6.7</td>
<td>35</td>
<td>97.6</td>
</tr>
<tr>
<td>3.0</td>
<td>6.7</td>
<td>60</td>
<td>98.2</td>
</tr>
<tr>
<td>3.0</td>
<td>6.7</td>
<td>60</td>
<td>95.1</td>
</tr>
<tr>
<td>3.5</td>
<td>5.8</td>
<td>20</td>
<td>87.1</td>
</tr>
<tr>
<td>3.5</td>
<td>5.8</td>
<td>25</td>
<td>87.5</td>
</tr>
<tr>
<td>3.5</td>
<td>5.8</td>
<td>30</td>
<td>90.0</td>
</tr>
<tr>
<td>3.5</td>
<td>6.7</td>
<td>20</td>
<td>86.0</td>
</tr>
<tr>
<td>3.5</td>
<td>6.7</td>
<td>25</td>
<td>91.2</td>
</tr>
<tr>
<td>3.5</td>
<td>6.7</td>
<td>30</td>
<td>92.4</td>
</tr>
</tbody>
</table>
of heating was increased in five minutes increments from 20 to 35 minutes with 10 minutes cooling before removal from the heating mantle. A definite improvement in extraction efficiency can be seen. For example, the pH 3.0 extractions containing a total quantity of 6.7 grams of NaCl increased from 90.4% E to 97.6% E as heating time was increased from 20 to 35 minutes. Since the data indicated a rising trend, it was felt that further increases in heating duration might further improve extraction efficiency. Rather than proceeding in five minute increments, heating time was increased to 60 minutes. The extractions were run at pH 3.0 and a total of 6.7 grams NaCl was added to each prior to separation. Three determinations were run under these conditions. The average of the three results was approximately the same as achieved at 35 minutes, 97.3% E average vs. 97.6% E indicating that further heating would not increase the extraction efficiency.

The effects of two different levels of salt concentration were also evaluated. The results are presented in Table IV. Total additions of 5.8 grams and 6.7 grams of NaCl were added to extractions under identical pH and heating conditions. Variation of the level of salt concentration gave inconsistent results, extractions with the lower salt level sometimes gave slightly higher extraction efficiencies, but the general trend is to higher extraction efficiency at the higher salting level.

As mentioned previously, the extractions were carried out at both pH 3.0 and 3.5 (Table V). The lower pH value gave consistently
Table IV
EFFECT OF SALT CONCENTRATION ON %E

<table>
<thead>
<tr>
<th>Heating (min.)</th>
<th>pH</th>
<th>%E at 5.8 g NaCl/25 ml aqueous</th>
<th>%E at 6.7 g NaCl/25 ml aqueous</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.0</td>
<td>92.6</td>
<td>90.4</td>
</tr>
<tr>
<td>25</td>
<td>3.0</td>
<td>93.3</td>
<td>93.8</td>
</tr>
<tr>
<td>30</td>
<td>3.0</td>
<td>94.7</td>
<td>96.5</td>
</tr>
<tr>
<td>20</td>
<td>3.5</td>
<td>87.1</td>
<td>86.0</td>
</tr>
<tr>
<td>25</td>
<td>3.5</td>
<td>87.5</td>
<td>91.2</td>
</tr>
<tr>
<td>30</td>
<td>3.5</td>
<td>90.0</td>
<td>92.4</td>
</tr>
</tbody>
</table>
Table V

EFFECT OF PH ON %E

<table>
<thead>
<tr>
<th>Heating (min.)</th>
<th>Total NaCl (g)</th>
<th>%E at pH 3.0</th>
<th>%E at pH 3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.8</td>
<td>92.6</td>
<td>87.1</td>
</tr>
<tr>
<td>25</td>
<td>5.8</td>
<td>93.3</td>
<td>87.5</td>
</tr>
<tr>
<td>30</td>
<td>5.8</td>
<td>94.7</td>
<td>90.0</td>
</tr>
<tr>
<td>20</td>
<td>6.7</td>
<td>90.4</td>
<td>86.0</td>
</tr>
<tr>
<td>25</td>
<td>6.7</td>
<td>93.8</td>
<td>91.2</td>
</tr>
<tr>
<td>30</td>
<td>6.7</td>
<td>96.5</td>
<td>92.4</td>
</tr>
</tbody>
</table>
higher results than those at pH 3.5. This may result from effects of higher ionic strength on the rate of hexaquochromium ion dissociation.

The conditions that appear to be optimum for use with the thiosalicylic-phthalic acid system would be 35 minutes heating, pH 3.0, and 6.7 grams of added salt. The extraction efficiencies of thiosalicylic acid, phthalic acid, and salicylic acid were compared under these conditions and were 96.4%, 91.7%, and 82.1% respectively. These results are in agreement with those from the preliminary extraction curves.

Several extractions were run as reagent blanks or to evaluate the quantity of chromium extracted by different reagents used in the extraction experiments. An extraction using only butanol as the organic layer but buffered with KHP gave an extraction efficiency of 88.1%. A reagent blank containing all components except chromium showed an absorbance equivalent to 0.1 ppm chromium which was judged negligible. Response equivalent to 0.5 ppm chromium was detected when only butanol and unbuffered chromium solution were carried through the extraction process. This indicates that CrCl$_3$ may be slightly soluble in butanol or there may have been incomplete separation of the aqueous and organic layers.

**MOLE RATIO EXPERIMENTS**

The nature of the extracted species was investigated by the mole ratio method of determining the number of ligands involved in forming a complex. Solutions of different ligand concentrations were reacted with a constant concentration of metal. If formation
constants are sufficiently large a plot of absorbance of the complex vs. ligand concentration will yield straight lines in the region of the plot where the ligand or metal is in large excess. These lines, when extrapolated, should intersect at the point where the ratio of the concentration of ligand to that of metal ion is equal to the combining ratio. This behavior results from the virtually quantitative formation of complex which occurs at large excess of either reagent. The absorbance curve itself falls away from the straight lines in the stoichiometric region of the plot since the degree of complex formation will be less than complete. The degree of deviation depends upon the magnitude of the formation constant. Mole ratio curves are presented for thiosalicylic, phthalic, and mixed ligands in Figures XI thru XIII.

Mole ratio plots obtained when either thiosalicylic acid or phthalic acid is the sole ligand indicate that a 2:1 complex is formed. This is in keeping with Aggett's findings with salicylic acid. It is assumed that the remaining sites in the coordination sphere are filled by H₂O molecules. Plots obtained when a varying ratio of thiosalicylic acid is reacted with a solution containing fixed amounts of phthalic acid and metal ion indicate an approximately linear variation with thiosalicylic acid concentration, indicating that a mixture of extractable species may form with the mixed extraction system. The least squares equation of the line is \( Y = 0.00344X + 0.0316 \).
FIGURE XI
MOLE RATIO PLOT
THIOSALICYLIC ACID
FIGURE XII
MOLE RATIO PLOT
PHTHALIC ACID
FIGURE XIII
MOLE RATIO PLOT
THIOSALICYLIC ACID VARIABLE
PHTHALIC ACID 1-1 MOLE RATIO

Absorbance at 550 nm vs. ligand solution (ml)

mole ratio
Thiosalicylic Acid
DISTRIBUTION RATIOS

Analyses of aliquots taken after collection of the total aqueous and organic layers were used, together with the determined volumes of the respective layers, in calculating distribution ratios for the extractions. These distribution ratios were then used to determine calculated values of extraction efficiency from the formula given in appendix 1. These calculated values of extraction efficiency were in good agreement with those obtained by comparison of chromium recovered from the organic layer with total chromium available for extraction. The values for thiosalicylic-phthalic acid extractions are presented in Table VI.
<table>
<thead>
<tr>
<th>Extraction Conditions</th>
<th>D</th>
<th>%E from D</th>
<th>%E from recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 minutes heating, pH 3.0</td>
<td>19.1</td>
<td>95.1</td>
<td>95.1</td>
</tr>
<tr>
<td>20 minutes heating, pH 3.5</td>
<td>8.12</td>
<td>88.9</td>
<td>86.3</td>
</tr>
<tr>
<td>20 minutes heating, pH 3.0</td>
<td>13.8</td>
<td>93.1</td>
<td>90.5</td>
</tr>
</tbody>
</table>
CONCLUSION

An efficient new method of chromium extraction has been demonstrated. The extraction efficiency of thiosalicylic-phthalic acid extraction systems has been shown to approach 100% when used in conjunction with a KHP buffer. Optimum pH and heating duration were found to be pH 3.0 and 35 minutes reflux time. The use of salting-out agents as an extraction aid was studied and the technique was found to enhance the extraction efficiency with the reagents studied in this work.

This research has demonstrated the need for further investigation in several areas. While the thiosalicylic-phthalic acid combination has been shown to be an effective extraction system for chromium(III), further work should be done to investigate its adaptation to real world analyses. Sensitivity, selectivity, and reproducibility of the extraction process should be studied before routine utilization of the method can begin. The ability of salt additions to enhance complex formation during the reflux step and the effects of different salts should also be investigated.
Appendix 1

Definitions

\[ D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \]

The distribution ratio is the ratio of the concentration of metal ion in the organic phase to that in the aqueous phase without regard to chemical state.

\[ \%E = \frac{[M]_{\text{org}} \text{ Vorg}}{[M]_{\text{org}} \text{ Vorg} + [M]_{\text{aq}} \text{ Vaq}} \times 100 = \text{extraction efficiency} \]

\[ \%E = \frac{100 \ D}{D + \frac{\text{Vol} \text{ aq}}{\text{Vorg}}} \text{ or } \frac{100 \ D}{D + 1} \text{ when Vaq} = \text{Vorg} \]

\[ K_a, \text{ acid dissociation constant} = \frac{[L^-][H^+]_{\text{aq}}}{[HL]_{\text{aq}}} \]

\[ K_{D,C} = \text{distribution of complex between phases} = \frac{[MLn]_{\text{org}}}{[MLn]_{\text{aq}}} \]

\[ K_{D,A} = \text{distribution of ligand acid between phases} = \frac{[HL]_{\text{org}}}{[HL]_{\text{aq}}} \]

\[ \beta = \text{formation constant of complex} = \frac{[MLn]_{\text{org}}}{[M^{n+}][L^-]^n} \]
also note that

\[ K_{ex} = \frac{[MLn]_{org} [H^+]^n}{[M^{n+}] [HL]^n_{org}} \]

\[ = K_D, C \frac{[MLn] [H^+]^n}{[MLn] [L^-]^n_{org} \beta [L^-]^n} \]

\[ = \frac{K_D, C [MLn] [H^+]^n}{[MLn] [L^-]^n_{org} \beta [L^-]^n} \]

\[ = \frac{K_D, C [MLn] [H^+]^n}{[MLn] [L^-]^n_{org} \beta [L^-]^n} \]

\[ = \frac{K_D, C [MLn] [H^+]^n}{[MLn] [L^-]^n_{org} \beta [L^-]^n} \]

\[ = \frac{K_D, C Ka^n}{\beta K_D', r} \]

\[ = (\frac{Ka}{K_D', r})^n K_D, C \beta \]

\[ \text{K_{ex} = \frac{[H^+]^n}{[HL]^n_{org}}} \]

\[ \text{D} = (\frac{Ka}{K_D', r})^n K_D, C \beta \left( \frac{[HL]^n_{org}}{[H^+]^n} \right) \]

\[ \text{from } K_D \text{ and } \beta = \frac{[MLn]}{[M^{n+}] [L^-]^n} \]

\[ \text{from } K_D, r = \frac{[HL]_{org}}{[HL]_{aq}} \]

\[ \text{from } Ka = \frac{[H^+] [L^-]}{[HL]} \]

\[ \text{from } D = (\frac{[Ka]}{K_D', r})^n K_D, C \beta \left( \frac{[HL]_{org}}{[H^+]^n} \right) \]

\[ \text{Appendix 249} \]
Appendix 3

Ionization of acids at pH 3.5

\[ a_o = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2} \]
\[ a_1 = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \]
\[ a_2 = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \]

The formulas given above were used to calculate percent ionization for the ligands at pH 3.5. The acid dissociation constants were taken from Table I.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( % H_2L )</th>
<th>( % HL^- )</th>
<th>( % L^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic Acid</td>
<td>19</td>
<td>81</td>
<td>2.0 \times 10^{-8}</td>
</tr>
<tr>
<td>Thiosalicylic Acid*</td>
<td>19</td>
<td>81</td>
<td>3.3 \times 10^{-4}</td>
</tr>
<tr>
<td>O-Phththalic Acid</td>
<td>16</td>
<td>82</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*K_1 equivalent to salicylic acid was assumed.
Appendix 4

The solution in which chromium (VI) would be reduced to chromium (III) contains 1 ml HClO₄ and 1 ml H₂SO₄ in a total volume of approximately 25 ml when the Na₂SO₃ solution is added. The pH of the solution at this point would be -0.07 ([H⁺] = 1.18 M) assuming complete dissociation of HClO₄ and of the first hydrogen of H₂SO₄. At this pH, 99% of the sulfite would be in the form of undissociated H₂SO₃. The following redox calculations indicate that chromium (VI) would be reduced by the sulfurous acid present to chromium (III) but not chromium (II).

\[3\text{H}_2\text{SO}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{SO}_4^{-2} + 12\text{H}^+ + 6\text{e} \quad E^0 = -0.20V^{51}\]

\[\text{Cr}_2\text{O}_7^{2-} + 6\text{e} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^0 = +1.33V^{52}\]

\[2\text{H}_2\text{SO}_3 + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \rightarrow 3\text{SO}_4^{2-} + 2\text{Cr}^{3+} + 4\text{H}_2\text{O} \quad E^0 = +1.113V\]

\[\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{-2} + 4\text{H}^+ + 2\text{e} \quad E^0 = -0.20V\]

\[2\text{Cr}^{3+} + 2\text{e} \rightarrow 2\text{Cr}^{2+} \quad E^0 = -0.38^{53}\]

\[\text{H}_2\text{SO}_3 + 2\text{Cr}^{3+} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{Cr}^{3+} + 4\text{H}^+ + 2\text{e} \quad E^0 = -0.58\]
FOOTNOTES


BIBLIOGRAPHY


