COMPOSITION AND CONCENTRATIVE PROPERTIES OF HUMAN URINE

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Abstract

This report defines the composition of typical human urine and presents experimental data on its chemical, physical, engineering and concentrative properties. The effects of chemical and electrolytic pretreatments used in aerospace applications for extraction of potable water are included. The results are presented in tables and plots of unsmoothed data, empirical equations, and tables of nominal values. Sample calculations and examples illustrating the consideration of these data in engineering design applications are included.
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COMPOSITION AND CONCENTRATIVE PROPERTIES OF HUMAN URINE

By David F. Putnam
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SUMMARY

This report defines the composition of typical human urine and presents experimental data on its chemical, physical, engineering, and concentrative properties. The effects of chemical and electrolytic pretreatments used in aerospace applications for extraction of potable water are included. The results are presented in tables and plots of unsmoothed data, empirical equations, and tables of nominal values. Sample calculations and examples illustrating the consideration of these data in engineering design applications are included.

INTRODUCTION

The reclamation and reuse of water from human urine is mandatory for long duration space missions due to the severe restrictions imposed on launch weight. Engineering studies show that the equivalent weight of most urine purification equipment is significantly lower than the weight of drinking water that would have to be launched as stored water, if no water recovery system were used (References 1 and 2).

The many different urine purification systems that are under investigation have at least one point in common: all must deal with urine that becomes progressively more concentrated as drinking water is extracted (References 3 through 13). It is clear, therefore, that knowledge of the chemical and physical properties of urine concentrates, for which there is very little reference information, is required for the satisfactory analysis and design of all urine-processing systems. It is hoped that the data reported here will fulfill this need.

The 68 chemical constituents that comprise over 99 percent of the solutes in urine are listed in decreasing order of concentration. A simplified analog of typical urine is presented, consisting of 42 chemical compounds. Data on
variations in urine composition are presented in terms of refractive index, specific conductivity, pH, total dissolved solids, chemical oxygen demand (standard and rapid methods), total Kjeldahl nitrogen, and total organic carbon. The electrolytic pretreatment of urine is described, a mass balance is presented, a discussion of the electrochemistry of the process is given, and a typical composition of electrolyzed urine is listed. The physical properties of urine concentrates were determined in the ranges 4 to 90 percent solutes and 70 to 140 degrees Fahrenheit. Both smoothed and unsmoothed data are presented in tables and plots, which are grouped together at the back of this report. The physical property data presented are the following:

- solute weight fraction
- solute to water ratio
- vapor pressure
- osmolality
- density
- osmolarity
- solute concentration
- osmotic pressure
- water concentration
- heat of vaporization
- heat of solution
- viscosity
- specific heat
- weight fraction of precipitated solids
- surface tension
- weight fraction of extracted water
- specific conductivity
- refractive index
- pH
SYMBOLS

C = solute concentration, g, of solutes per ml of urine
COD = chemical oxygen demand, g/l or mg/l
CO₂D = chemical oxygen demand (rapid method), g/l or mg/l
Cₚ = specific heat, BTU/lb x ° F
CW = water concentration, g of water per ml of urine
Hₜ = differential heat of dilution, BTU per lb of water increase
Hₛ = differential heat of solution, BTU per lb of solute increase
Hᵤ = differential heat of vaporization of urine, BTU per pound of urine
k = specific conductivity, mmho-cm⁻¹ or μmho-cm⁻¹
L = differential heat of vaporization of urine, BTU per pound of water evaporated
Lᵤ = differential heat of vaporization of urine, BTU per pound of urine
Lₜ = differential heat of vaporization of water, BTU per pound of water evaporated
M = apparent average molecular weight of solute particles as calculated from vapor pressure data and Raoult's Law
N = number of moles of solvent = \( \frac{Wₜ}{18} \)
n = number of moles of solute particles = \( \frac{Wₛ}{M} \)
n₁ = refractive index at 70° F relative to air for sodium yellow light
O = osmolality, apparent g-moles of solute particles per 1000 g of water
Or = osmolarity, apparent g-moles of solute particles per liter of urine
p = vapor pressure of urine concentrate, psia
p* = vapor pressure of pure water, psia
\( p\text{H} \) = hydrogen ion concentration, \( \log_{10} \) of the reciprocal of the molar concentration of hydrogen ions (H⁺)

\[
10^{-p\text{H}} = \frac{\text{g-moles of hydrogen ions (H⁺)}}{\text{liter}}
\]

\( R \) = gas constant, \( 8.3144 \frac{\text{Joules}}{\text{g-mole} \times \text{°K}} \)

\( S \) = entropy, \( \text{BTU/lb} \times \text{°F} \)

\( T \) = temperature, degrees Rankine, Fahrenheit, or Kelvin

\( \text{TDS} \) = total dissolved solids, \( \text{g/Kg or mg/Kg} \)

\( \text{TKN} \) = total Kjeldahl nitrogen, \( \text{g/l or mg/l} \)

\( \text{TOC} \) = total organic carbon, \( \text{g/l or mg/l} \)

\( \bar{v} \) = molar volume of water, \( 18 \frac{\text{cm}^3}{\text{g-mole}} \)

\( \text{Ww} \) = weight of solvent, \( \text{g} \)

\( \text{Wp} \) = weight of precipitate, \( \text{g} \)

\( \text{Ws} \) = weight of solutes, \( \text{g} \)

\( \text{Wu} \) = weight of urine, \( \text{g} \)

\( x \) = solute weight fraction, \( \text{g of solutes per g of urine} \)

\( 1 - x \) = water weight fraction, \( \text{g of water per g of urine} \)

\( x_0 \) = original solute weight fraction, \( \text{g of solutes per g of urine, initially before concentration} \)

\( 1 - x_0 \) = original water weight fraction, \( \text{g of water per g of urine, initially before concentration} \)

\( y \) = weight fraction of extracted water, \( \text{g of water extracted from urine during concentration per g of initial water content before concentration} \)

\( 1 - y \) = weight fraction of unextracted water, \( \text{g of water in urine concentrate per g of initial water content before concentration} \)

\( \gamma \) = surface tension, \( \text{dynes-cm}^{-1} \)

\( \mu \) = dynamic viscosity, centipoise

\( \pi \) = osmotic pressure, psia

\( \rho \) = density, \( \text{g of urine per ml of urine} \)
COMPOSITION OF HUMAN URINE

The composition of human urine has been studied by many investigators and the quantities of 158 different chemical constituents are summarized in the NASA Bioastronautics Data Book (Reference 14). These constituents are broadly categorized as electrolytes, nitrogenous compounds, vitamins, hormones, organic acids, and miscellaneous organic compounds. The 68 constituents that have individual maximum concentrations exceeding 10 mg/l are listed in Table I in decreasing order of concentration. These constituents add up to about 36,800 mg/l in typical urine. The remaining 90 compounds total approximately 250 mg/l.

For engineering analysis purposes in water reclamation technologies, an abbreviated list of compounds is in most cases more than adequate to characterize human urine. This is not to suggest that there is any substitute for using real urine in the development and testing of water recovery subsystems; rather, that it is convenient, and sufficiently accurate for most analyses, to use a simplified version of the real thing. An analog for real urine, consisting of 42 compounds, is presented in Table II. The concentrations listed are considered to be typical, and are based on the information in Table I, the measurements presented elsewhere in this report, and the results of numerous chemical analyses of urine made over the last 10 years in the course of developing water recovery subsystems. The 42 out of 158 compounds in Table II account for over 98 percent of the total solute concentration in urine. For most analyses and calculations, Table II should serve as a convenient starting point to develop an even more simplified analog such as Table III, which shows the major categories of (1) inorganic salts, (2) urea, (3) organic compounds, and (4) organic ammonium salts broken down into content of carbon, nitrogen, oxygen, hydrogen, and organic sulfur.

Some measurements that help to broadly categorize urine are presented in Table IV. The measurements were made on 16 different batches of raw, unconcentrated, nonpretreated urine, each containing about 40 liters composed from 20 to 30 male subjects. The total dissolved solids (TDS) of the batches ranged from 24.8 grams per kilogram to 37.1 grams per kilogram.
The measurements selected were considered to be the most significant available for broadly categorizing urine. In addition to the directly measured values of $n_i$, $k$, pH, TDS, CO$_2$D, COD, TKN, and TOC, there are columns of nitrogen and carbon as determined by gas analysis in the electrolytic pretreatment process (see ELECTROLYTIC PRETREATMENT OF HUMAN URINE). The agreement between the two different methods of determination is close for nitrogen, but not so close for carbon. The data in Table IV are plotted in Figures 1 through 8 against TDS. Although a generally increasing trend with increasing TDS is apparent for each parameter except pH, there is considerable deviation from mean values. It is not known how much of the deviation is due to actual variations in the level of the measured quantities, and how much is due to interferences and side reactions involved in the method of measurement. The particular significance of each measurement is discussed below.

Refractive Index ($n_i$)

The refractive index measurements in this section were made at 70°F with a Bausch and Lomb refractometer calibrated for sodium yellow light relative to air. For a discussion of refractive index of aqueous solutions, see References 15 and 16. For refractive index data on common binary solutions see References 16 and 17. The refractive index has been found to have a straight-line correlation (Figure 12) with solute weight fraction ($x$) for most species in binary solution. In addition, for many species the effects of solute weight fraction on refractive index are additive.

Specific Conductivity ($k$)

Specific conductivity is a function of the ionic species present in water. If the amount and identity of each ionic solute is known, then the specific conductivity of a solution can be calculated, as there is a definite relationship between ion concentration and specific conductivity for individual species. The specific conductivity, calculated for the urine listed in Table II, assuming an activity coefficient of 0.74 for each inorganic salt (Reference 17, p. D-93), is 18.0 mmho-cm$^{-1}$ for the inorganic salts, and approximately 1.5 mmho-cm$^{-1}$ for the organic ammonium salts, for a total of 19.5 mmho-cm$^{-1}$. This is very close to the values found in real urine (see Figure 2).
pH

pH is a measure of $\text{H}^+$ and $\text{OH}^-$ ions. Usually, in the case of urine, low pH is caused by unbuffered organic acids, and high pH is caused by unbuffered ammonium.

Total Dissolved Solids (TDS)

TDS was determined in the same manner as solute weight fraction, i.e., by drying samples at room temperature with a purge flow of -40°F dew point air. TDS is reported in grams per kilogram of solution and is equal to solute weight fraction times 1000. The TDS measurement cannot be expected to match a theoretical calculation of total dissolved solids based on a quantitative knowledge of the species present in urine, because of factors such as volatilization of organic matter, mechanically occluded water, water of hydration, hygroscopic properties of the residue, heat induced chemical decomposition, and oxidation effects. In the case of urine, drying at room temperature minimizes the loss of high vapor pressure solutes such as NH$_4$HCO$_3$, HCl, formic acid, amines and phenols; and results in a TDS figure that is slightly higher than the theoretical value due mainly to water of hydration. As a rule of thumb, it is felt that the TDS value for raw urine in grams per kilogram is approximately equal to the theoretical concentration in grams per liter.

Rapid Method for Chemical Oxygen Demand ($\text{CO}_2$D)

In this method, a microsample is injected into a heated combustion tube (see Reference 18) through which $\text{CO}_2$ is flowing. Reducing materials react with the $\text{CO}_2$ to form CO, which is measured by an infrared analyzer. A generalized equation for oxidation by a combustion process for urine organics is

$$C_a H_b N_c O_d + \frac{n}{2}O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O + \frac{c}{2}N_2$$  \hspace{1cm} (1)

The oxidizing equation for $\text{CO}_2$ is

$$C_a H_b N_c O_d + mCO_2 \rightarrow (m+a)CO + \frac{b}{2}H_2O + \frac{c}{2}N_2$$  \hspace{1cm} (2)
When both Equations (1) and (2) are balanced in respect to oxygen, then \( n = m + a \) and the number of moles of CO produced in Equation (2) is equal to the number of oxygen atoms required in Equation (1). The results are reported as grams per liter of oxygen and are termed "C02D".

The mixture of organics in urine per Table II are approximately represented by the equation \( \text{C}_2 \text{H}_6 \text{N}_2 \text{O}_2 \). The oxidation of this mixture by CO2 would be

\[
\text{C}_2 \text{H}_6 \text{N}_2 \text{O}_2 + 3 \text{CO}_2 \rightarrow 5 \text{CO} + 3 \text{H}_2\text{O} + \text{N}_2
\]  

Therefore, in this case, if complete oxidation occurred with no interferences, the total organics in urine would be approximately equal to \( 90/80 \times \text{C02D} \).

The efficiency of oxidation for a number of compounds as reported in Reference 18 is as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{CO}_2 \text{D}, \text{mg/l} )</th>
<th>Oxidation Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcd</td>
<td>Found</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>246</td>
<td>239</td>
</tr>
<tr>
<td>Benzonic acid</td>
<td>250</td>
<td>248</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>250</td>
<td>244</td>
</tr>
<tr>
<td>Glycine</td>
<td>250</td>
<td>248</td>
</tr>
<tr>
<td>Urea</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>p-Nitroaniline</td>
<td>250</td>
<td>244</td>
</tr>
<tr>
<td>Phenol</td>
<td>245</td>
<td>216</td>
</tr>
<tr>
<td>Sucrose</td>
<td>248</td>
<td>215</td>
</tr>
<tr>
<td>Acetone</td>
<td>173</td>
<td>145</td>
</tr>
<tr>
<td>Ethanol</td>
<td>235</td>
<td>200</td>
</tr>
<tr>
<td>Methanol</td>
<td>238</td>
<td>205</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>250</td>
<td>204</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>250</td>
<td>274</td>
</tr>
</tbody>
</table>

Chemical Oxygen Demand (COD)

Chemical oxygen demand is often used as indication of the total organic content of water (Reference 19). It is a measure of the amount of
dichromate that is reduced by oxidation of the organics. Typical COD values for three organic materials are as follows:

<table>
<thead>
<tr>
<th>Item</th>
<th>COD</th>
</tr>
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<tbody>
<tr>
<td>Lactose</td>
<td>0.84 g/g</td>
</tr>
<tr>
<td>Glucose</td>
<td>1.07 g/g  (Theoretical, Reference 19)</td>
</tr>
<tr>
<td>Potassium Acid Phthalate</td>
<td>1.18 g/g  (Theoretical, Reference 19)</td>
</tr>
</tbody>
</table>

The oxidation of most organic compounds by dichromate is 95 to 100 percent of the theoretical value. However, ammonia, urea, benzene, toluene, and pyridine are among the compounds that are not oxidized by dichromate. Since urine contains large amounts of urea, ammonia and amines, its COD values would be expected to run considerably below the total organic content of urine, and the data presented in Table IV bear this out.

Total Kjeldahl Nitrogen (TKN)

Total Kjeldahl nitrogen (Reference 19) measures organic nitrogen in the trinegative state and includes ammonia nitrogen. TKN would be expected to measure essentially all of the nitrogen in raw urine. When the organics in raw urine are approximately represented by the equation $C_2H_6N_2O_2$, then the total organics would be approximately equal to $\frac{90}{28} \times$ TKN.

Nitrate and nitrite nitrogen are not measured by TKN and are not present to any appreciable extent in raw urine. However, in electrolyzed urine there can be high levels of nitrate present, and in this case TKN does not indicate total nitrogen.

Total Organic Carbon (TOC)

The total organic carbon measurement was made with a Beckman Model 915 Total Organic Carbon Analyzer (see Reference 20). This instrument complies with the ASTM tentative method D2579-T for the determination of organic carbon in water and waste water. A small-size water sample is swept into a catalytic combustion tube (950°C) where all carbonaceous material is oxidized to carbon dioxide. After removal of the water vapor, the CO$_2$ is introduced into an infrared analyzer sensitized to measure CO$_2$. A parallel sample is then injected into a second combustion tube
maintained at a lower temperature (150°C). By this procedure only inorganic carbonates and dissolved CO₂ are liberated. They are swept into the infrared analyzer where they are separately determined. The difference between the total carbon dioxide and the inorganic carbon dioxide is indicative of the organic carbon present in the sample. The method measures essentially all of the carbon in urine. When the organics in urine are approximately represented by the equation \( \text{C}_2\text{H}_6\text{N}_2\text{O}_2 \), then the total organics in urine would be approximately equal to \( \frac{90}{24} \times \text{TOC} \).
ELECTROLYTIC PRETREATMENT OF HUMAN URINE

By passing sufficient electricity through human urine, most of the dissolved organic compounds can be converted to hydrogen, oxygen, nitrogen, and carbon dioxide, which are outgassed, leaving behind a semipurified urine that contains primarily inorganic salts. These residual inorganic salts can be removed by electrodialysis to produce potable water. The complete water recovery process is termed electropurification and a typical mass balance is shown in Figure 9. The overall electrochemical reaction is approximately represented as follows:

\[ X_3O + 2 C_2H_6N_2O_2 + 11 H_2O \rightarrow X_3O_4 + 17 H_2 + 2N_2 + 20_2 + 4CO_2 \]  

In this equation, \( X_3O \) represents the inorganic compounds in raw urine, \( C_2H_6N_2O_2 \) represents the organic compounds in raw urine, and \( X_3O_4 \) represents the inorganic compounds in electrolyzed urine. \( X \) represents all atoms other than C, H, N, and O and is considered to have an atomic weight of approximately 30, which is about average for the composition of Table 11.

The mechanism for the overall electrochemical reaction is not known. However, it is felt that chemical reactions involving hypochlorite, chlorate, perchlorate, and perhaps both nascent chlorine and nascent oxygen are of prime importance. In actual practice, a batch of urine consisting of approximately 4 liters is circulated through an electrolysis cell operating at a current density in the range 200 to 300 mA/cm² until the TOC, COD, and TKN are each reduced to less than 100 mg/L. The transient behavior of the urine during electrolysis is shown in Figures 10, 11, 12, 13, 14 and 15. These plots are estimates for the typical urine described in Tables II and III, and are based on composited data from approximately 16 test runs. An estimate of the salts remaining after electrolysis is shown in Table V. Essentially all organic material is gone. The organic sulfur is converted to sulfate and most of the original chloride is converted to chlorate and perchlorate. Figures 16, 17, 18 and 19 characterize electrolyzed urine in terms of refractive index, specific conductivity, pH, and TDS respectively. Considerable deviation from mean values is evident.
Figures 10 through 15 give some insight into the dynamics of the organic removal process. In the first few minutes of electrolysis there is an induction period in which the chloride level drops about 10% (Figure 10). Conversion of chloride to hypochlorite according to the following reaction is indicated:

\[
\text{Anode: } 6\text{Cl}^- - 6e \rightarrow 6\text{Cl} \\
\text{Cathode: } 6\text{Na}^+ + 6\text{HOH} + 6e \rightarrow 6\text{NaOH} + 3\text{H}_2 \\
\text{Mixing: } 6\text{NaOH} + 3\text{Cl}_2 \rightarrow 3\text{NaOCl} + 3\text{NaCl} + 3\text{H}_2\text{O}
\]

During the first 3 hours of electrolysis, the outgassing of oxygen is low (Figure 14), indicating that little if any excess water is being electrolyzed. The ratio of nitrogen to carbon (Figure 15) is higher than the average value for urine, indicating that urea and other high-nitrogen organics are being oxidized in preference to low- and zero-nitrogen organics such as the organic acids. The fact that COD, which does not include urea, is decreasing (Figure 10) indicates that other organics besides urea are also being oxidized. The primary chemical reaction appears to be hypochlorite oxidation, which, for urea, is mainly as follows:

\[
\text{Oxidation: } \text{H}_2\text{NCONH}_2 + 3\text{NaOCl} \rightarrow \text{CO}_2 + \text{N}_2 + 3\text{NaCl} + 2\text{H}_2\text{O}
\]

The overall reaction, combining Equations (5), (6), (7), and (8) would be as follows:

\[
\text{Overall reaction: } \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{N}_2 + 3\text{H}_2
\]

Between hour 3 and hour 4 the chloride level drops, indicating a higher concentration of hypochlorite and the preferential oxidation of a new group of organic compounds. The decline in pH (Figures 10 and 15) indicates that ammonium ions are also being removed, leaving the organic acids unbuffered. By hour 4 the organic nitrogen (TKN, Figure 10) has dropped to almost zero and the nitrogen to carbon ratio (Figure 15) is below the average value. The nitrogen compounds that remain in solution as zero TKN is approached were identified as mainly nitrogen trichloride, \(\text{NCl}_3\), and nitrate ion, \(\text{NO}_3^-\).
NC13 is detected by TKN, but NO3⁻ is not. NC13 is an end product of the hypochlorite oxidation of urea (Reference 21). For simplicity, it is not shown in Equation (8), which represents the primary reaction of hypochlorite with urea. NC13 can be converted to NO3⁻ by hypochlorite as follows:

\[ \text{NC13} + \text{HOCI} + 2\text{H}_2\text{O} \rightarrow \text{NO3}^- + 4\text{Cl}^- + 5\text{H}^+ \]  

It was found that in low voltage electrolysis (current density < 2 mA/cm²) large concentrations (~5 g/l) of NO3⁻ did occur, but in high voltage electrolysis (current density > 150 mA/cm²) the NO3⁻ concentration remained low (<40 mg/l). It was also found that the organic acids that remain in solution at this point in the process are mainly formic (HCOOH) and acetic (CH₃CO₂H) acids. These free aliphatic acids are the products of hypochlorite and N-chloro compound reactions with the organic materials other than urea. Low-voltage electrolysis does not remove these residual organic acids. The addition of a catalyst during low voltage electrolysis reduced the residual NO3⁻ level, but did not reduce the level of residual organic acids.

Between hour 4 and hour 5 of high voltage electrolysis, the chloride level continues to drop (Figure 10), indicating a continuing conversion to hypochlorite. Also, the rapid drop in refractive index as it is compared to TDS (Figure 12) indicates a conversion of hypochlorite to chlorate, which was verified by laboratory analysis. Chlorate can be produced by the following reaction that occurs in acid solutions (see References 22 and 23):

\[ \text{CIO}^- + 2\text{HOC1} \rightarrow \text{ClO}_3^- + 2\text{HCl} \]  

Chlorate can also be produced by anodic oxidation (References 22 and 23) as follows:

\[ 6\text{ClO}^- + 3\text{H}_2\text{O} - 6\text{e} \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 6\text{H}^+ + 3\text{O} \]  

The increase in oxygen production (Figure 14) would argue that Equation (12) predominates. Also during this period the pH (Figure 15) begins to rise, indicating that the residual organic acids are being oxidized. This oxidation process might involve the nascent oxygen that is produced in Equation (12), or it might be a direct electrolytic decomposition at the anode.
It probably does not involve the chlorate ion, which is not as good an oxidizer as hypochlorite. Also, nitrogen continues to be evolved (Figure 14) indicating the removal of unidentified residual nitrogen-containing compounds.

Between hour 5 and hour 6 the pH completes its rise to pH = 7, and the organic level falls to below 500 mg/l (Figure 10). Since nearly all of the chloride was converted to chlorate by the beginning of the fifth hour, the n\textsubscript{i} vs TDS data (Figure 12) indicate that chlorates are being converted to perchlorates by anodic oxidation as follows:

\[
\text{ClO}_3^- + \text{H}_2\text{O} - 2e^- \rightarrow \text{ClO}_4^- + 2\text{H}^+
\]  

Between hour 6 and hour 7 the organic level is reduced to less than 100 mg/l, while more perchlorates are produced. At hour 7 the organic level is low enough that subsequent processing by electrodialysis produces water that meets all of the NAS/NRC chemical potability standards (Reference 24).
PHYSICAL PROPERTIES OF HUMAN URINE CONCENTRATES

The physical properties reported in this section were determined for the mixed urine of 40 to 50 male subjects over a period of several months. Seven batches of urine, containing 19 liters per batch, were each concentrated by evaporation to approximately 200 milliliters, at which point the liquors of similarly pretreated batches were mixed and concentrated further. The physical properties were measured at discrete intervals during the concentration process. The unsmoothed data are presented in Table VI. Four different chemical pretreatments were investigated as follows:

- \( \text{H}_2\text{SO}_4 + \text{CrO}_3 \)
- \( \text{H}_2\text{SO}_4 + \text{CrO}_3 + \text{CuSO}_4 \)
- \( \text{Ca(ClO)}_2 \)
- Electrolytic (see ELECTROLYTIC PRETREATMENT OF HUMAN URINE)

Pretreatments are used in most urine processing systems (References 2 and 25) to stabilize urine with respect to microbes, odors, and free ammonia. These four pretreatments are the most widely used. Physical property data were not obtained for untreated urine because bacterial action always developed within the first few days of the one-to-two-month period in which the progressive concentration of the urine and physical measurements were made. This bacterial action resulted in the decomposition of urea and the evolution of large amounts of ammonia.

Most of the physical properties are not sensitive to the first three pretreatments, in which less than 10 g per liter of chemical are involved. Only precipitate, viscosity, and pH are noticeably affected. The electrochemical pretreatment which converts most of the organic material in urine to useful cabin gases has a noticeable impact on many of the concentrative properties, but not on vapor pressure and the other colligative properties.

Symbols are assigned in Table VI to each batch of urine, and these symbols are used consistently through this section. Deviations in the data can be readily determined from the individual plots that are presented in each section.
Nominal values for the physical properties, which are intended for use in engineering calculations are presented in Tables VII, VIII, and IX. The following examples are given to illustrate the usefulness of these data and to underscore several often-neglected design considerations.

Example 1, Vapor Compression System

In a vapor compression system, latent heat is conserved by compressing the evolved water vapor to a higher pressure. This allows it to condense at a temperature that is higher than the boiling temperature of urine, thereby making possible the transfer of latent heat from the condensing vapor to the boiling urine. This thermodynamic process is illustrated on a T-S diagram in Figure 20 and is summarized as follows:

1-2: Boiling of urine, heat received from condensing vapor

2-4: Compression of vapor from boiling pressure to a higher condensing pressure (2-4 is for boiling of pure water; 2'-4' and 2''-4'' are for boiling of urine concentrates)

4-5-6: Cooling and condensing of vapor, heat rejected to boiling urine.

As the urine, which is fed to and contained within a vapor compression system, becomes more and more concentrated due to the extraction of water, its vapor pressure decreases as shown in Table VIII. The pressure ratio required to raise the pressure of the evolved vapor to a level at which its condensing temperature is just equal to the boiling temperature of the concentrated urine (illustrated in Figure 20 by the paths 2'-3' and 2''-3'') is easily calculated from Table VIII. It is simply the ratio of the vapor pressure at $x = 0$ to that at $x$. For any $x$, this ratio is very nearly the same in the range $80^\circ F$ to $140^\circ F$. The ratio is plotted in Figure 21.

Combining the data in Figure 21 with those in Figure 49 results in Figure 22, a plot that shows the pressure ratio versus the weight fraction of extracted water.

Figure 22 is useful when evaluating the point at which it is no longer beneficial to increase pressure ratio and hence compressor weight and power for the sake of obtaining higher water recovery efficiencies. When
evaluations such as these are made, other factors that also directly or indirectly influence pressure ratio and are a function of the amount of water extracted, such as scaling due to precipitate formation and changes in transport properties, must also be evaluated.

Example 2, Vacuum Distillation System

The designer is concerned with establishing optimum boiling and condensing temperatures on the basis of heat and mass transfer with a vacuum distillation system, as with any distillation system including vapor compression. The rise in the boiling point of urine that accompanies higher concentrations must not be ignored. The increase in boiling point as a function of water extracted is shown in Figure 23 and is obtained by combining data from Figures 30 and 49.

Example 3, Reverse Osmosis System

In a reverse osmosis system, the pressure applied to the urine must exceed the osmotic pressure in order to achieve a reverse osmotic flow of water. As water is extracted, the osmotic pressure of the remaining concentrate increases as shown in Figure 24, which was obtained by combining Figures 38 and 49.

The required increase in osmotic pressure to achieve a higher water recovery efficiency represents an increase in weight and power, so for any mission there is an optimum operating pressure.

Example 4, Miscellaneous Considerations

Several designers have proposed urine distillation systems in which urine would be continually fed into an evaporator compartment and precipitates would be continually separated and withdrawn. Presumably this proposition is based on the mistaken belief that urine behavior is similar to that of a binary solution such as sodium chloride and water, in which the brine does not concentrate beyond the solubility limit of sodium chloride. However, urine does not behave like this. Due to the presence of many highly soluble and even some liquid species such as citric, formic, and lactic acids, urine
continues to get more and more concentrated as water is extracted, even as certain species are being precipitated. This behavior is indicated in Figure 47.

In most of the systems that have been proposed for extracting water from urine, the extraction process is discontinued before 100 percent of the water is removed, i.e., before complete dryness is reached. This leaves the task of transferring the mother liquor, including entrained precipitates, from the water removal area to a holding or storage area. The viscosity and precipitate data contained here should be helpful in the design of transfer systems, and density data should aid in sizing the volume required for storing the mother liquor.

The calculations required to obtain these kinds of precipitate and volume information are illustrated in the following example.

Assume urine with the following initial conditions:

\[
\text{Pretreatment: } \text{H}_2\text{SO}_4 + \text{CrO}_3 + \text{CuSO}_4
\]

\[x_0 = 0.042\]

\[\rho_0 = 1.012\]

Calculate the amount of precipitate contained in the urine concentrate slurry that remains after extraction of 98 percent of the water from a liter of urine with the above listed initial conditions. Also calculate the slurry's volume.

From Figure 48 for \(y = 0.98; x = 0.665\)

From Figure 32 for \(x = 0.665; \rho = 1.312\)

From Figure 47 for \(x = 0.665; \frac{W_P}{W_{S_0}} = 0.11\)

\[W_{U_0} = \rho_0 V_o = 1.012 (1000) = 1012 \text{ g}\]

\[W_{S_0} = x_0 W_{U_0} = 0.042 (1012) = 42.5 \text{ g}\]

\[W_P = \frac{W_P}{W_{S_0}} W_{S_0} = 0.11 (42.5) = 4.675 \text{ g}\]
\[ V_p = \frac{W_p}{\rho_p} = \frac{4.675}{1.470} = 3.18 \text{ ml} \]

(from Figure 32 at \( x = 1.0, \rho_p = 1.470 \))

\[ W_s = W_{so} - W_p = 42.5 - 4.675 = 37.82 \text{ g} \]

\[ W_u = \frac{W_s}{x} = \frac{37.85}{1.665} = 23.0 \text{ g} \]

\[ V_u = \frac{W_u}{\rho} = \frac{56.84}{1.312} = 43.32 \text{ ml} \]

Weight of precipitate = \( W_p = 4.675 \text{ g} \)

Weight of slurry = \( W_u + W_p = 56.84 + 4.675 = 61.52 \text{ g} \)

Volume of slurry = \( V_u + V_p = 43.32 + 3.18 = 46.50 \text{ ml} \)

Similar calculations for other pretreatments and various degrees of water extraction enabled construction of Figures 25 and 26.

Systems that require the removal and storage of a mother liquor need a simple way of monitoring the progress of the water extraction process to determine the proper end point. Refractive index, Figure 50 deviates less between different batches of urine and different pretreatments than any other physical property. In addition, the measurement is relatively easy to make and requires only a smear of sample. It would be a relatively simple, direct, and accurate means of monitoring and controlling water recovery processes.

**Solute Weight Fraction**

Solute weight fraction is the total weight of dissolved substances in urine per unit weight of urine. It does not include precipitated solids. As urine is concentrated, some of the original solids are normally precipitated, as shown in Figure 47. The solute weight fraction includes only those species which remain in solution. It was determined by drying an aliquot of concentrate to approximately a \(-40^\circ\) F dew point with a dry air purge at room temperature. With this technique there is a minimal loss of high vapor pressure solutes such as \( \text{NH}_3, \text{CO}_2, \text{HCl} \), formic acid, amines, and phenols. Solute weight fraction is the property against which all of the other physical properties are correlated.
Vapor Pressure

Vapor pressure was determined with an Othmer vapor-liquid equilibrium still (Reference 26). The data were smoothed in a two-step procedure in which Raoult's law was utilized. First, the apparent average molecular weight of solute particles, M, was calculated with Raoult's equation and the values were plotted against the boiling temperature, T, of the urine concentrate. The apparent average molecular weight is equal to the true average molecular weight of solute particles only at infinite dilution where intermolecular actions between solute particles is minimal. The term "particle" includes both molecules and ions and is a necessary distinction because a mole of ions lowers vapor pressure as much as a mole of undissociated molecules. The equation used to compute M is derived as follows:

Raoult's law states that the ratio of the amount of vapor pressure lowering to the vapor pressure of the pure solvent is equal to the ratio of the number of moles of solute particles to the number of moles of solution:

$$\frac{p^* - p}{p^*} = \frac{n}{N + n}$$

Rearranging terms:

$$\frac{p}{p^*} = \frac{N}{N + n}$$

$$\frac{p^* - p}{p} = \frac{n}{N} = \frac{Ws/M}{Ww/18} = \frac{x}{1 - x} \frac{18}{M}$$

$$M = 18 \frac{x}{1 - x} \frac{p}{p^*} - p$$

where:

- $p^*$ = vapor pressure of solvent
- $p$ = vapor pressure of solution
- $Ws$ = weight of solute
\[ W_w = \text{weight of solvent} \]
\[ N = \text{number of moles of solvent} = \frac{W_w}{18} \]
\[ n = \text{number of moles of solute particles} = \frac{W_s}{M} \]
\[ M = \text{apparent average molecular weight of solute particles} \]
\[ x = \text{solute weight fraction} \]
\[ T = \text{boiling temperature of urine} \]

The values for \( x \), \( p \), and \( T \) were measured. \( p^* \) was obtained from published data (Reference 27).

For most urine samples the plot of \( M \) vs \( T \) had a small negative slope with the following mean value:

\[ \frac{dM}{dT} = -0.1145 \]

The second step in the two-step procedure for smoothing vapor pressure data was carried out next. From the plots of \( M \) vs \( T \), \( M \) at 100° F was plotted against the solute fraction, \( x \), as shown in Figure 27.

The nominal line shown in Figure 27 was then fitted, and points from it were used as input to a computer program that calculated the nominal values of vapor pressure and the other colligative properties that are presented in Tables VII, VIII and IX.

The following equations were used:

\[ P = \frac{p^*}{\left( \frac{18}{M} \frac{x}{1-x} \right) + 1} \]

\[ M_T = M_{100} - 0.1145 \ (T-100) \]

where:

\[ T = \text{degrees Fahrenheit} \]

and all other parameters are as previously defined.
This method of smoothing vapor pressure data is advantageous for computing the colligative properties as compared to standard smoothing techniques such as plotting of Dühring lines and graphing ln p versus ln p*

In addition to the table of nominal vapor pressures, Table VII, the smoothed vapor pressure data are presented in three familiar forms in Figures 28, 29, and 30. In figure 31, vapor pressure data are compared to the smoothed values and to the measured values of urea and sodium chloride solutions.

Density

Density was calculated from specific gravity measurements made with precision grade hydrometers. The data are plotted in Figure 32.

Most of the chemically treated urines scatter around a mean line within approximately ± 1 1/2 percent. This mean line is described by the following equation:

\[ \rho = 0.4775 x + 0.99325 \]

where:

- \( \rho \) = density, g of urine per ml of urine
- \( x \) = solute weight fraction, g of solutes per g of urine

The density of the electrolytically treated urine is greater for a given solute fraction than chemically treated urine due to a substantial loss of organic solutes. It is expressed by the following equation (for the lower curve in Figure 32, which is for treatment at low current density):

\[ \rho = 0.6110 x + 0.9904 \]

where:

- \( \rho \) = density, g of urine per ml of urine
- \( x \) = solute weight fraction, g of solutes per g of urine

The density of urine treated electrolytically at high current density is not a straight line. The curve in Figure 32 may be used.
Solute Concentration

The solute concentration, \( C \), is the weight of solutes per unit volume of urine and is calculated as follows:

\[
C = \rho x
\]

where:

\( C \) = solute concentration, g of solutes per ml of urine
\( \rho \) = density, g of urine per ml of urine
\( x \) = solute weight fraction, g of solutes per g of urine

The nominal variation of solute concentration at 70° F with solute weight fraction is shown in Figure 33.

Water Concentration

The water concentration, \( C_w \), is the weight of water per unit volume of urine. \( C_w \) is equal to the difference between density and solute concentration, and is calculated as follows:

\[
C_w = \rho - C = \rho (1 - x)
\]

where:

\( C_w \) = water concentration, g of water per ml of urine
\( \rho \) = density, g of urine per ml of urine
\( C \) = concentration, g of solutes per ml of urine
\( x \) = solute weight fraction, g of solutes per g of urine

The nominal variation of water concentration at 70° F with solute weight fraction is shown in Figure 34.
Solute to Water Ratio

The solute to water ratio is the weight of solutes per unit weight of water, and is equal to:

\[ \frac{x}{1 - x} \]

where:

\( \frac{x}{1 - x} \) = g of solute per g of water

\( x \) = solute weight fraction, g of solute per g of urine

\( 1 - x \) = water weight fraction, g of water per g of urine

The variations of solute to water ratio with solute weight fraction is independent of the pretreatment used and is shown in Figure 35.

Osmolality

Osmolality is analogous to molality. The difference is that in osmolality, the apparent average molecular weight of solute particles as determined by measuring vapor pressure depression and applying Raoult’s law, is used instead of the average molecular weight of solute molecules. The distinction between particles and molecules is important; so too is the relationship of osmolality to vapor pressure depression. For further discussion see the Vapor Pressure paragraphs.

Osmolality is defined as the number of apparent g-moles of solute particles (as calculated from vapor pressure data) per 1,000 g of solvent:

\[ O = \frac{n}{Ww} \times 1000 = \frac{Ws/M}{Ww} \times 1000 \]

\[ = \frac{x}{1 - x} \times \frac{1000}{M} = \frac{p^* - p}{p} \times \frac{1000}{18} \]
where:

\[ O = \text{osmolality, apparent g-moles of solute particles per 1000 g of water} \]

\[ n = \text{number of solute particles} = \frac{W_s}{M} \]

\[ W_s = \text{weight of solute, g} \]

\[ M = \text{apparent average molecular weight of solute particles} \]

\[ W_w = \text{weight of water, g} \]

\[ x = \text{solute weight fraction, g of solutes per g of urine} \]

\[ p^* = \text{vapor pressure of water, psia} \]

\[ p = \text{vapor pressure of urine, psia} \]

The variation of osmolality at 100° F with solute weight fraction is shown in Figure 36.

**Osmolarity**

Osmolarity is analogous to molarity in the same way osmolality is analogous to molality. Refer to Osmolality paragraphs.

Osmolarity is defined as the number of apparent g-moles of solute particles (as calculated from vapor pressure data) per liter of solution:

\[ O_r = \frac{n}{W_u} \rho 1000 = \frac{W_s/M}{W_u} \rho 1000 = \frac{x \rho}{M} 1000 = \frac{C}{M} 1000 \]

\[ = \frac{p^* - p}{\rho} \frac{1000}{18} \rho (1 - x) \]

\[ = \rho (1 - x) O = (\rho - C) O = C w O \]

where:

\[ O_r = \text{osmolarity, apparent g-moles of solute particles per liter of urine} \]

\[ O = \text{osmolality, apparent g-moles of solute particles per 1,000 g of water} \]
\( n \) = number of moles of solute particles = \( \frac{W_s}{M} \)

\( W_s \) = weight of solute, g

\( M \) = apparent average molecular weight of solute particles

\( W_u \) = weight of urine, g

\( \rho \) = density of urine, g of urine per ml of urine

\( C \) = solute concentration, g of solutes per ml of urine

\( C_w \) = water concentration, g of water per ml of urine, = \( \rho - C \)

\( x \) = solute weight fraction, g of solutes per g of urine

\( p^w \) = vapor pressure of water, psia

\( p \) = vapor pressure of urine, psia

The variation of osmolarity at 100° F with solute weight fraction is shown in Figure 37 for chemically pretreated urine.

**Osmotic Pressure**

Osmotic pressure is estimated from the vapor pressure data. In practice such estimates are found to approximate closely experimental values to osmolarities of 5 and beyond (Reference 28). The osmotic pressure was calculated at 100° F as follows:

\[
\pi = a \frac{RT}{\nu} \ln \left( \frac{p^w}{p} \right)
\]

\[
= 20,836 \ln \left( \frac{p^w}{p} + 1 \right)
\]

where:

\( \pi \) = osmotic pressure, psia

\( R \) = gas constant, 8.3144 \( \frac{\text{Joules}}{\text{g-mole} \cdot \text{°K}} \)

\( T \) = temperature, 311°K (100° F)
\( \bar{v} = \text{molar volume of water, } 18 \frac{\text{cm}^3}{\text{g-mole}} \)

\( a = 1.4504 \times 10^{-5} \frac{\text{psia}}{\text{dyne-cm}^2} \)

\( p^* = \text{vapor pressure of water at } 100^\circ \text{F, psia} \)

\( p = \text{vapor pressure of urine at } 100^\circ \text{F, psia} \)

The variation of osmotic pressure with solute weight fraction is shown in Figure 38.

**Differential Heat of Vaporization**

The following relationship between vapor pressure and heat of vaporization is derived (Reference 29) by integration of the Clausius-Clapeyron equation:

\[
\ln p = \frac{L}{L^*} \ln p^* + c
\]

where:

\( p = \text{vapor pressure of urine, psia} \)

\( p^* = \text{vapor pressure of water, psia} \)

\( L = \text{differential heat of vaporization of urine, BTU per lb of water evaporated} \)

\( L^* = \text{heat of vaporization of pure water, BTU per lb of water evaporated} \)

\( c = \text{constant of integration} \)

The nominal values for \( L \) that are shown in Table IX were calculated by evaluating the above equation, over the range \( 80^\circ \text{F} \) to \( 144^\circ \text{F} \), at two different pressures separated by an increment corresponding to \( 4^\circ \text{F} \). The calculation is made as follows:

\[
\ln p_2 = \frac{L}{L^*} \ln p_2^* + c
\]

\[
\ln p_1 = \frac{L}{L^*} \ln p_1^* + c
\]
subtracting:

\[ \ln p_2 - \ln p_1 = \frac{L}{L^*} (\ln p_2^* - \ln p_1^*) \]

\[ \frac{L}{L^*} = \frac{\ln(p_2/p_1)}{\ln (p_2^*/p_1^*)} \]

The differential heat of vaporization, \( L \), is the heat required to remove a unit quantity of water from urine with an infinitesimal increase in concentration. The differential heat of vaporization, \( Lu \), which would be required to vaporize all of the water in a unit quantity of urine without changing concentration is calculated as follows:

\[ Lu = (1 - x) L \]

where:

- \( Lu \) = differential heat of vaporization of urine, BTU/lb of urine
- \( L \) = differential heat of vaporization of urine, BTU/lb of water
- \( 1 - x \) = weight fraction of water, lb of water per lb of urine

Water cannot, of course, be vaporized from urine without a change in concentration. The heat required to effect an evaporative increase in concentration is called the integral heat of vaporization, and can be evaluated by using an average value for the differential heat of vaporization in the interval of concentration under consideration.

A computer program was used to calculate nominal values of \( L \) and \( Lu \) using vapor pressure and enthalpy data for pure water (Reference 27) at 4° F increments, and the equations for vapor pressure that are given in the Vapor Pressure paragraphs. Nominal values are tabulated in Table IX. The variation with solute weight fraction for one temperature is shown in Figure 39.
Differential Heat of Solution

The differential heat of solution and the differential heat of dilution are defined in Reference 28 as follows:

Differential heat of solution is the heat absorbed when a unit quantity of solute is added to a very large quantity of solution at a specified concentration.

Differential heat of dilution is the heat absorbed when a unit quantity of solvent is added to a very large quantity of solution at a specified concentration.

The relationship between these two quantities is readily derived by considering the case in which solvent and solute are added in a proportion that causes no change in concentration. For this case the net change in energy of the solution is zero; therefore:

\[ \Delta W_w \Delta h_w + \Delta W_s \Delta h_s = 0 \]

and for no change in concentration, the solvent and solute must be added in the following proportion:

\[ \frac{\Delta W_w}{\Delta W_s} = \frac{1 - x}{x} \]

These two expressions combine as follows:

\[ \Delta h_s = -\Delta h_w \frac{1 - x}{x} \]

where:

- \( \Delta h_s \) = differential heat of solution, BTU per lb of solute increase
- \( \Delta h_w \) = differential heat of dilution, BTU per lb of water increase
- \( \Delta W_w \) = water increase, lb
- \( \Delta W_s \) = solute increase, lb
- \( \frac{1 - x}{x} \) = ratio of water to solutes, lb of water per lb solute
Applying the first law of thermodynamics to the process of vaporizing water from a urine solution the following relationship is derived:

\[ \text{H}_w = L^{\#} - L \]

where:

- \( \text{H}_w \) = differential heat of dilution, BTU per lb of water increase
- \( L^{\#} \) = heat of vaporization of pure water, BTU per lb of water evaporated
- \( L \) = differential heat of vaporization of urine, BTU per lb of water evaporated

The above expressions were used to compute the nominal values of \( H_s \) and \( H_w \) that are presented in Tables VII and IX. Their variation with solute weight fraction is shown in Figure 40 and 41 respectively.

Specific Heat

The specific heat is presented in Figure 42 and was obtained from Reference 30. Nominal values are listed in Table VII.

Surface Tension

Surface tension was measured by the capillary rise method (Reference 31). Nominal values of surface tension are presented in Table VII. The data are plotted in Figure 43.

Specific Conductivity

The specific conductivity was measured with a small platinum electrode cell of about 5 ml capacity with a cell constant of 10 cm\(^{-1}\). Nominal values of specific conductivity are presented in Table VII. The data are plotted in Figure 44.
Viscosity

Viscosity was measured with an Ostwald viscometer (Reference 28 and 32). Nominal values are presented in Table VII. The data are plotted in Figures 45 and 46. The following empirical relationships were found:

For \( x < 0.5 \):

All pretreatments:

\[
\mu = 0.9 e^{\frac{3}{2}\left(\frac{x}{1-x}\right)}
\]

For \( x > 0.5 \):

Ca(ClO)\(_2\) pretreatment:

\[
\mu = \frac{8}{7} e^{\frac{5}{4}\left(\frac{x}{1-x}\right)}
\]

H\(_2\)SO\(_4\) + CrO\(_3\) pretreatment:

\[
\mu = 1.8 e^{\frac{4}{5}\left(\frac{x}{1-x}\right)}
\]

where:

\( \mu \) = dynamic viscosity, centipoise

\( x \) = solute weight fraction, g of solutes per g of urine

\( 1-x \) = water fraction, g of water per g of urine

Weight Fraction of Precipitated Solids

The amount of precipitate was determined by filtering all suspended and precipitated solids from a urine sample of known size and composition. The amount of dried precipitate is reported as a fraction of the original solute content. The following definition is made:

\[
\text{Weight Fraction of Precipitated Solids} = \frac{W_P}{W_{SO}} = \text{g of dry precipitate per g of original solute content}
\]
The data are presented in Figure 47. There is little variance in the $\text{H}_2\text{SO}_4 + \text{CrO}_3$ pretreatment data. $\text{Ca(ClO)}_2$ and electrolytic pretreatment data have a wider spread. Nominal values are presented in Table VII.

Weight Fraction of Extracted Water

The weight fraction of extracted water is defined as the amount of water removed from urine during dehydration per unit weight of the original water content. The following algebraic relationship applies:

$$y = 1 - \left(1 - \frac{W_p}{W_{so}}\right) \frac{x_o}{1 - x_o} \frac{1 - x}{x}$$

where:

- $y$ = weight fraction of extracted water, g of water extracted from urine per g of original water content
- $x$ = solute weight fraction, g of solutes per g of urine
- $1 - x$ = water weight fraction, g of water per g of urine
- $x_o$ = original solute weight fraction, g of original solutes per g of original urine
- $1 - x_o$ = original water weight fraction, g of original water per g of original urine
- $\frac{W_p}{W_{so}}$ = weight fraction of precipitated solids, g of dry precipitate per g of original solute content
- $1 - \frac{W_p}{W_{so}}$ = weight fraction of remaining solutes, g of solutes per g of original solute content

The data are presented in Figure 48. Nominal values are presented in Table VII and in Figure 49, which shows the weight fraction of extracted water as a function of solute weight fraction for $x_o = 0.04$. 

32
Refractive Index

The refractive index determinations were made at 70° F with an Abbe refractometer calibrated for sodium yellow light relative to air. The data are plotted in Figure 50 and show a straight-line relationship between refractive index and solute weight fraction up to about \( x = 0.51 \). At this point the slope of the line increases abruptly. Refractive index may be used to calculate nominal values of \( x \) with the following empirical equations. Nominal values of \( n_i \) are listed in Table VII.

For \( x < 0.51 \):

\[
x = 6.29371 n_i - 8.38545
\]

For \( x > 0.51 \):

\[
x = 4.12655 n_i - 5.32242
\]

where:

\( x \) = solute weight fraction, g of solute per g of urine

\( n_i \) = refractive index at 70° F relative to air for sodium yellow light

The refractive index is often plotted in the following form as shown in Figure 51:

\[
\frac{1}{\rho} \frac{n^2 - 1}{n^2 + 2}
\]

where:

\( \rho \) = density, g of urine per ml of urine

\( n_i \) = refractive index at 70° F relative to air for sodium yellow light

There are theoretical reasons (Reference 14) why this parameter should exhibit linear dependence on solute weight fraction. It is interesting that except for the high current density electrolytic pretreatment, the parameter
remains within ±4 percent of the value 0.2020, for $0 < x < 0.90$, and within this narrow range it varies in straight-line relationships.

**pH**

pH was measured electrometrically at 70°F with a Beckman Expanded Scale pH meter. The data show that pH is primarily a function of initial pH and pretreatment. Concentration causes pH to change but little from its initial value. The data are plotted in Figure 52.
REFERENCES


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<tr>
<td>Uropepsin (as Tyrosine)</td>
<td>HO·C₆H₄·C₂H₃(NH₂)·CO₂H</td>
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<td>181.2</td>
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<td>Imidazole Derivatives</td>
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<td>130</td>
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<td>Citrulline</td>
<td>NH₂CONH(CH₂₃)₂·CH⁺·(NH₂)·CO₂H</td>
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<td></td>
<td>175.2</td>
<td>0</td>
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<td>Threonine</td>
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<td></td>
<td>119.1</td>
<td>10</td>
<td>120</td>
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<tr>
<td>Lysine</td>
<td>(NH₂)₂C₆H₅·CO₂H</td>
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<td></td>
<td>146.2</td>
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<tr>
<td>m-Hydroxyhippuric Acid</td>
<td>C₆H₄COHC(OH·CH₂·COOH)</td>
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<td></td>
<td>195.2</td>
<td>1</td>
<td>100</td>
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<td>p-Hydroxyphenyl-Hydrocrylic Acid</td>
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### Table I
CONSTITUENTS OF HUMAN URINE EXCEEDING 10 mg/l. FROM REFERENCE 12 (Concluded)

<table>
<thead>
<tr>
<th>Item</th>
<th>Formula</th>
<th>Weight mg/l</th>
<th>Range mg/l</th>
<th>Solubility Limit In A Binary Solution g/100g H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminoisobutyric Acid</td>
<td>H₂N·CH₂&gt;CH·CHOOH</td>
<td>103.1</td>
<td>3</td>
<td>120</td>
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<tr>
<td>Inositol</td>
<td>C₆H₁₂O₆</td>
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<td>5</td>
<td>100</td>
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<td>Formic Acid</td>
<td>H·CO₂H</td>
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<td>20</td>
<td>90∞</td>
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<tr>
<td>Urobilin</td>
<td>C₃₃H₄₀O₆N₄</td>
<td>588.7</td>
<td>7</td>
<td>90</td>
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<tr>
<td>Tyrosine</td>
<td>HO·C₂H₄·C₅H₅(NH₂)·CO₂H</td>
<td>181.2</td>
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<td>70.04</td>
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<td>Pyruvic Acid</td>
<td>CH₅·CO·CO₂H</td>
<td>88.1</td>
<td>2</td>
<td>70∞</td>
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<td>Albumin</td>
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<td>7</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Asparagine</td>
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<td>132.1</td>
<td>20</td>
<td>70 3.1</td>
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<tr>
<td>Tryptophan</td>
<td>C₆H₄·NH·C·CH·C·C₅H₅(NH₂)·CO₂H</td>
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<td>60 25</td>
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<td>Ketones (as Acetone)</td>
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<td>Serine</td>
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<td>50 20.5</td>
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<td>Glycocyamine</td>
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<td>Proline</td>
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<td>40 V.S.</td>
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<td>Arginine</td>
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<td>&lt;7</td>
<td>40 15</td>
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<td>Ascorbic Acid</td>
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<td>40 V.S.</td>
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<td>Bilirubin</td>
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<td>Valine</td>
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<td>Phenylalanine</td>
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<td>Allantoin</td>
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<td>25</td>
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<td>Guanidinoacetic Acid</td>
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<td>15∞</td>
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<td>13 V.S.</td>
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<td>Dehydroascorbic Acid</td>
<td>C₆H₆O₆</td>
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</table>

Other Organics: 285
## Table II

AN ANALOG REPRESENTING THE COMPOSITION OF TYPICAL HUMAN URINE

<table>
<thead>
<tr>
<th>ITEM</th>
<th>FORMULA</th>
<th>FORMULA WEIGHT</th>
<th>AMOUNT mg/L</th>
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<td><strong>INORGANIC SALTS</strong></td>
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<td>Sodium Chloride</td>
<td>NaCl</td>
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<td>MgCO₃</td>
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<td>Potassium Phosphate</td>
<td>K₃PO₄</td>
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<td>Calcium Phosphate</td>
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<td>H₂NCONH₂</td>
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<td>Creatinine</td>
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<td>Uropepsin (as Tyrosine)</td>
<td>HO-C₄H₄-C₂H₃(NH₂)₂-CO₂H</td>
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<td>Creatine</td>
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<td>Androsterone</td>
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<td>1-Methylhistidine</td>
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<td>p-Hydroxysphenyl - hydrocrylic acid</td>
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<tr>
<td>Imositol</td>
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<td>70</td>
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<tr>
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<td>C₃₃H₄₀O₈N₄</td>
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<td>63</td>
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<tr>
<td>Tyrosine</td>
<td>HO-C₆H₄-C₂H₃(NH₂)₂-CO₂H</td>
<td>181.2</td>
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<tr>
<td>Asparagin</td>
<td>HO₂C·CH(NH₂)·CH₂-CONH₂</td>
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<td>Organics less than 50 mg/L</td>
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<td>Ammonium:</td>
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<td>Hippurate</td>
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<td>1,250</td>
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<tr>
<td>Urate</td>
<td>NH₄C₆H₅O₇·N₄</td>
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<td>518</td>
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<tr>
<td>Lactate</td>
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<tr>
<td>L-Glutamate</td>
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<td>Formate</td>
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<td>NH₄CH₃·CO·CO₂</td>
<td>88.1</td>
<td>44</td>
</tr>
<tr>
<td>Oxalate</td>
<td>(NH₄)₂C₅O₄</td>
<td>124.0</td>
<td>37</td>
</tr>
<tr>
<td><strong>Total Solutes</strong></td>
<td></td>
<td></td>
<td>37,057</td>
</tr>
</tbody>
</table>
### Table III

**SUMMARY OF C, N, O, H AND ORGANIC S IN TYPICAL HUMAN URINE**

<table>
<thead>
<tr>
<th>Item</th>
<th>Amount (mg/l)</th>
<th>C (12.0) (mg/l)</th>
<th>N (14.0) (mg/l)</th>
<th>O (16.0) (mg/l)</th>
<th>H (1.0) (mg/l)</th>
<th>S (32.1) (Organic) (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic Salts</td>
<td>14,157</td>
<td>100</td>
<td>0.0</td>
<td>1,877</td>
<td>7</td>
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</tr>
<tr>
<td>Urea</td>
<td>13,400</td>
<td>2,880</td>
<td>6,253</td>
<td>3,573</td>
<td>893</td>
<td>0</td>
</tr>
<tr>
<td>Organic Compounds</td>
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<td>2,466</td>
<td>1,211</td>
<td>1,231</td>
<td>347</td>
<td>134</td>
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<tr>
<td>Organic Ammonium Salts</td>
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<td>1,630</td>
<td>659</td>
<td>1,576</td>
<td>266</td>
<td>0</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>37,057</strong></td>
<td><strong>6,076</strong></td>
<td><strong>3,123</strong></td>
<td><strong>8,237</strong></td>
<td><strong>1,513</strong></td>
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### Table IV

**SIGNIFICANT MEASUREMENTS THAT BROADLY CATEGORIZE HUMAN URINE**

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>TDS (g/Kg)</th>
<th>K (cm)</th>
<th>pH</th>
<th>CO₂ D (g/l)</th>
<th>COD (g/l)</th>
<th>TKN (g/l)</th>
<th>TOC (g/l)</th>
<th>N By Gas Analysis (g/l)</th>
<th>C By Gas Analysis (g/l)</th>
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<tr>
<td>1</td>
<td>36.5</td>
<td>1.383</td>
<td>6.7</td>
<td>17.6</td>
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<td>2</td>
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<td>6.74</td>
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<tr>
<td>3</td>
<td>33.4</td>
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<td>19.6</td>
<td>19.9</td>
<td>6.30</td>
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<tr>
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<td></td>
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<tr>
<td>5</td>
<td>29.1</td>
<td>1.384</td>
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<td>22.0</td>
<td>21.0</td>
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<tr>
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<td>6.5</td>
<td>19.6</td>
<td>21.8</td>
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<td>26.4</td>
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<td>24.0</td>
<td>10.3</td>
<td>7.81</td>
<td>7.50</td>
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<td>-</td>
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<td>5.51</td>
<td>3.62</td>
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### Table V

**AN ANALOG REPRESENTING THE SALTS REMAINING AFTER ELECTROLYTIC PRETREATMENT OF TYPICAL HUMAN URINE**

<table>
<thead>
<tr>
<th>Item</th>
<th>Formula</th>
<th>Formula Weight</th>
<th>Amount (mg/l)</th>
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</thead>
<tbody>
<tr>
<td>Sodium Chloride</td>
<td>NaCl</td>
<td>58.4</td>
<td>1,542</td>
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<tr>
<td>Sodium Chloride</td>
<td>NaClO₃</td>
<td>106.5</td>
<td>5,314</td>
</tr>
<tr>
<td>Sodium Perchlorate</td>
<td>NaClO₄</td>
<td>122.5</td>
<td>7,436</td>
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<tr>
<td>Potassium Phosphate</td>
<td>KO₃PO₄</td>
<td>338.6</td>
<td>776</td>
</tr>
<tr>
<td>Potassium Sulfate</td>
<td>K₂SO₄</td>
<td>174.3</td>
<td>4,497</td>
</tr>
<tr>
<td>Potassium Nitrate</td>
<td>KNO₃</td>
<td>101.1</td>
<td>162</td>
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<td>Magnesium Chloride</td>
<td>Mg₈Cl₂O₃·6H₂O</td>
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<tr>
<td>Potassium Phosphate</td>
<td>K₃PO₄</td>
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<td>Calcium Phosphate</td>
<td>Ca₃(PO₄)₂</td>
<td>310.2</td>
<td>62</td>
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</table>

*Total: 22,477*
### PHYSICAL PROPERTIES OF URINE CONCENTRATES

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<th>Symbol</th>
<th>Batch No.</th>
<th>Pretreatment</th>
<th>x</th>
<th>a</th>
<th>K</th>
<th>pH</th>
<th>γ</th>
<th>µ</th>
<th>CP</th>
<th>M</th>
<th>W</th>
<th>ΔT at 120°F</th>
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</thead>
<tbody>
<tr>
<td>Δ 3</td>
<td>H2SO4 = 2.57 g/l</td>
<td>0.04174</td>
<td>---</td>
<td>24.0</td>
<td>2.3</td>
<td>1.012</td>
<td>---</td>
<td>0.057</td>
<td>---</td>
<td>---</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CO2 = 0.63 g/l</td>
<td>0.1128</td>
<td>1.549</td>
<td>55.2</td>
<td>2.3</td>
<td>1.046</td>
<td>57.0</td>
<td>1.06</td>
<td>---</td>
<td>64.4</td>
<td>0.0073</td>
<td>0.687</td>
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<tr>
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<td>H2O = 2.56 g/l</td>
<td>0.2297</td>
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<td>1.106</td>
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<td>72.1</td>
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<td>0.3193</td>
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<td>1.150</td>
<td>47.4</td>
<td>1.86</td>
<td>---</td>
<td>65.7</td>
<td>0.0218</td>
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<td>γ 2</td>
<td>H2SO4 = 2.57 g/l</td>
<td>0.3510</td>
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<td>21.3</td>
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<td>1.010</td>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>0</td>
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<td>0.016</td>
<td>0.936</td>
<td>0.0229</td>
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<tr>
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<td>H2O = 2.56 g/l</td>
<td>0.3750</td>
<td>1.389</td>
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<td>1.169</td>
<td>45.2</td>
<td>2.21</td>
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<td>1.270</td>
<td>42.9</td>
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<td>63.3</td>
<td>0.0567</td>
<td>0.973</td>
<td>0.0219</td>
</tr>
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<td>Ω 3</td>
<td>H2SO4 = 2.26 g/l</td>
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<td>56.3</td>
<td>---</td>
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<td>0.0201</td>
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<tr>
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<td>CO2 = 0.06 g/l</td>
<td>0.04006</td>
<td>1.339</td>
<td>23.1</td>
<td>2.4</td>
<td>1.015</td>
<td>68.0</td>
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<td>56.3</td>
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<td>H2O = 2.56 g/l</td>
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<td>68.0</td>
<td>2.4</td>
<td>1.071</td>
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<td>76.0</td>
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<td>55.9</td>
<td>---</td>
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<td>1.226</td>
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<td>0.0208</td>
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<td>1.369</td>
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<td>45.1</td>
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<td>0.0276</td>
</tr>
<tr>
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<td>and after treatment</td>
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<td>3.6</td>
<td>1.429</td>
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Table VI
PHYSICAL PROPERTIES OF URINE CONCENTRATES (Continued)
Table VI

PHYSICAL PROPERTIES OF URINE CONCENTRATES (Continued)

Smoothed Data From Reference 30

| Batch Symbol | Batch No. | Pretreatment | x | n | K mmho cm⁻¹ | pH | ρ g/mL | γ dyne cm⁻¹ | μ Centipoise | Cₚ at 73°F | M at 100°F | Wₓ₂ / W₀₂ | γ | ΔT at 120°F Deg. F |
|--------------|-----------|--------------|---|---|-------------|----|--------|-------------|--------------|------------|------------|-------------|----------|---------------|-------------|
| None         | 0.05      | ---          | 25.0 | --- | 52.0        | 0.983 | ---    | ---         | ---          | ---        | ---        | ---          | ---      | ---           |
| Littman data | 0.06      | ---          | 1.024 | --- | 1.05        | 0.930 | ---    | ---         | ---          | ---        | ---        | ---          | ---      | ---           |
| (See Ref. 30) | 0.10      | ---          | 1.024 | --- | 1.23        | ---    | ---    | ---         | ---          | ---        | ---        | ---          | ---      | ---           |
|               | 0.16      | ---          | 1.097 | --- | 1.23        | 41.4   | ---    | ---         | ---          | ---        | 0.2051     | ---          | ---      | ---           |
|               | 0.17      | ---          | 1.097 | --- | 41.4        | ---    | ---    | ---         | ---          | ---        | 0.2051     | ---          | ---      | ---           |
|               | 0.20      | ---          | 1.097 | --- | 41.4        | 0.2042 | ---    | 2.2         | ---          | 2.2        | ---        | ---          | ---      | ---           |
|               | 0.30      | ---          | 1.097 | --- | 1.66        | 0.2039 | ---    | 4.5         | ---          | 4.5        | 0.2039     | 8.2          | ---      | ---           |
|               | 0.31      | ---          | 1.149 | --- | 2.37        | 0.2030 | ---    | 8.2         | ---          | 8.2        | 0.2030     | 14.8        | ---      | ---           |
|               | 0.40      | ---          | 1.193 | --- | 47.8        | ---    | ---    | 8.2         | ---          | 8.2        | ---        | 8.2          | ---      | ---           |
|               | 0.43      | ---          | 1.193 | --- | 8.2         | ---    | ---    | 8.2         | ---          | 8.2        | ---        | 8.2          | ---      | ---           |
|               | 0.50      | ---          | 1.345 | --- | 1.66        | 0.2051 | ---    | 14.8        | ---          | 14.8       | 0.2051     | ---          | ---      | ---           |
|               | 0.56      | ---          | 1.345 | --- | 30.4        | ---    | ---    | 30.4        | ---          | 30.4       | 30.4       | ---          | ---      | 30.4          |
|               | 0.60      | ---          | 1.432 | --- | 43.4        | ---    | ---    | 43.4        | ---          | 43.4       | 43.4       | ---          | ---      | 43.4          |
|               | 0.66      | ---          | 1.510 | --- | 9.96        | ---    | ---    | 9.96        | ---          | 9.96       | 9.96       | ---          | ---      | 9.96          |
**PHYSICAL PROPERTIES OF HUMAN URINE CONCENTRATES**

*(Nominal Values)*

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### Table VIII

**VAPOR PRESSURE OF HUMAN URINE CONCENTRATES**  
**NOMINAL VALUES, psia**  

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**SOLUTE WEIGHT FRACTION**  

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**WEIGHT FRACTION**

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**TABLE IX**

**TABLE HEADINGS**

\[ x = \text{solute weight fraction, g of solutes per g of urine} \]

\[ L/L^* = \text{ratio of heat of vaporization of urine to heat of vaporization of pure water} \]

\[ Lu = \text{differential heat of vaporization of urine, BTU/lb of urine} \]

\[ Hw = \text{differential heat of dilution, BTU/lb of water increase} \]

\[ Hs = \text{differential heat of dilution, BTU/lb of solute increase} \]

\[ L = \text{differential heat of vaporization of urine, BTU/lb of water evaporated} \]
Table IX
DIFFERENTIAL HEATS OF VAPORIZATION, SOLUTION, AND DILUTION (NOMINAL VALUES)

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TEMPERATURE OF URINE CONCENTRATE = 82.0

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TEMPERATURE OF URINE CONCENTRATE = 86.0

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**TEMPERATURE OF URINE CONCENTRATE = 98.0**

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**TEMPERATURE OF URINE CONCENTRATE = 102.0**

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### Table IX
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**TEMPERATURE OF URINE CONCENTRATE = 110.0**
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TEMPERATURE OF URINE CONCENTRATE = 122.0

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TEMPERATURE OF URINE CONCENTRATE = 126.0
### Table IX
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**Temperature of Urine Concentrate = 130.°C**

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**Temperature of Urine Concentrate = 134.°C**
### Table IX

**DIFFERENTIAL HEATS OF VAPORIZATION, SOLUTION, AND DILUTION (NOMINAL VALUES) (Continued)**

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**TEMPERATURE OF URINE CONCENTRATE = 138.0**

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**TEMPERATURE OF URINE CONCENTRATE = 142.0**

55
Figure 1. Refractive Index of Human Urine

TDS, TOTAL DISSOLVED SOLIDS, \( \text{mg/L} \)
TDS, TOTAL DISSOLVED SOLIDS, g/kg

Figure 2. Specific Conductivity of Human Urine
Figure 3. pH of Human Urine
Figure 4. Chemical Oxygen Demand of Human Urine (Rapid Method)
Figure 5. Chemical Oxygen Demand of Human Urine
Figure 6. Total Kjeldahl Nitrogen of Human Urine
Figure 7. Total Organic Carbon of Human Urine
Figure 8. Ratio of Nitrogen to Carbon in Human Urine
ALL WEIGHTS IN GRAMS

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| TOTALS | 1012.01 | 4.96 | 8.12 | 36.81 | 943.94 | 6.86 | 12.32 |

Figure 9. Mass Balance for Water Recovery From Typical Human Urine by Electropurification
Figure 10. CO\textsubscript{2}D, COD, TKN, TOC, Cl\textsuperscript{-}, and pH of Urine During Electrolytic Pretreatment
Figure 11. TDS and $n_i$ of Urine During Electrolytic Pretreatment
Figure 12. $n_\text{r}$ Versus TDS of Urine During Electrolytic Pretreatment
Figure 13. Optical Density of Urine During Electrolytic Pretreatment
Figure 14. Composition of Gas Output During Electrolytic Pretreatment
Figure 16. Ratio of Nitrogen to Carbon in Evolved Gas During Electrolytic Pretreatment
Figure 16. Refractive Index of Electrolyzed Urine
Figure 17. Specific Conductivity of Electrolyzed Urine
Figure 18. pH of Electrolyzed Urine

TDS, TOTAL DISSOLVED SOLIDS, g/kg
Figure 19. Final Versus Initial TDS of Electrolyzed Urine
Figure 20. T-S Diagram of Vapor Compression Process
Figure 21. Ratio of the Vapor Pressure of Pure Water to the Vapor Pressure of Urine Concentrate
Figure 22. Pressure Ratio as a Function of the Weight Fraction of Extracted Water
Figure 23. Boiling Point Rise as a Function of the Weight Fraction of Extracted Water
Figure 24. Osmotic Pressure as a Function of the Weight Fraction of Extracted Water
Figure 25. Volume of Urine Concentrate Slurry as a Function of the Weight Fraction of Extracted Water
Figure 26. Weight Fraction of Precipitated Solids as a Function of the Weight Fraction of Extracted Water
Figure 27. Apparent Average Molecular Weight of Urine Solute Particles
Logarithmic Plot of the Vapor Pressure of Urine Concentrates Versus the Vapor Pressure of Pure Water

Figure 28.
Figure 29. Semilogarithmic Plot of the Vapor Pressure of Urine Concentrates Versus the Reciprocal of the Boiling Temperature
Boiling Point Rise as a Function of Boiling Temperature, Condensing Temperature, and Solute Weight Fraction

Figure 30.
Figure 31. Boiling Point Rise of Urine Concentrate
Figure 32. Density of Urine Concentrate
Figure 33. Solute Concentration of Urine Concentrate
Figure 34. Water Concentration of Urine Concentrate
Figure 35. Solute to Water Ratio of Urine Concentrate
Figure 36. Osmolality of Urine Concentrate
Figure 37. Osmolarity of Urine Concentrate
Figure 38. Osmotic Pressure of Urine Concentrate
Figure 39. Differential Heat of Vaporization of Urine Concentrate
X. SOLUTE WEIGHT FRACTION

Figure 40. Differential Heat of Solution of Urine Concentrate
Figure 41. Differential Heat of Dilution of Urine Concentrate
Figure 42. Specific Heat of Urine Concentrate
Figure 43. Surface Tension of Urine Concentrate
Figure 44. Specific Conductivity of Urine Concentrate
Figure 45. Viscosity of Urine Concentrate

A. Viscosity at 70°F, Centipoise

x, Solute Weight Fraction
Figure 46. Viscosity as a Function of the Solute to Water Ratio
Figure 47. Weight Fraction of Solids Precipitated from Urine
Figure 48. Weight Fraction of Water Extracted From Urine
Figure 49. Weight Fraction of Extracted Water Versus Solute Weight Fraction

Y, WEIGHT FRACTION OF EXTRACTED WATER, (X₀ = 0.04)
Figure 51. Linear Dependence of $\rho^{-1}(n_1^2 - 1)/(n_1^2 + 2)$ on Solute Weight Fraction
Figure 52. pH of Urine Concentrates