OPTIMIZATION OF CHLORINATION PARAMETERS TO REDUCE THE FORMATION OF TRIHALOMETHANES IN DRINKING WATERS OF PUERTO RICO

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ABSTRACT

In 1974, trihalomethanes (chloroform, bromoform, bromodichloromethane, and dibromochloromethane) were discovered to be formed during the disinfection step of drinking water if free chlorine was the disinfectant. This led USEPA (United States Environmental Protection Agency) to amend the National Interim Primary Drinking Water Regulations to include a maximum contaminant level of 100 µg/L (ppb) for total trihalomethanes (TTHMs) in water. In Puerto Rico, the presence of trihalomethanes, potentially carcinogenic substances, in drinking water is a matter of serious concern for the general public, industry and government agencies. A better understanding is needed of the chlorination parameters which affect the formation of trihalomethanes.

In this work, we identified those operational variables involved in the chlorination of drinking waters which influence the formation on THMs, using raw waters from different geographical areas of Puerto Rico. They were found to be: non-volatile total organic carbon (NVTOC), pH, the ratio of applied chlorine dose to NVTOC, and bromide ion concentration. A factorial experiment was carefully designed
with the purpose of ascertaining the effect of those variables on total trihalomethanes formed during the chlorination process.

Pilot plant water filtration and chlorination facilities were designed and built in order to implement our multivariate analysis of the process. Analytical facilities were developed to routinely analyze water for THMs precursors, partially identified as humic and fulvic acids (characterized in terms of non-volatile total carbon, NVTOC) and bromide ion (Br⁻).

A highly significant regression model was developed relating TTHMs formation to the operational variables of the chlorination process. Residual chlorine, a measure of disinfection effectiveness, was also measured and correlated to the same variables. The two correlations developed provide a useful tool for minimization of THMs formation while guaranteeing proper disinfection.
RESUMEN

En 1974 se descubrió la presencia de trihalometanos (cloroformo, bromoformo, bromodiclórometano y dibromoclorometano) en aguas potables, formados durante el proceso de desinfección cuando se usaba cloro como desinfectante. Esto motivó a la Agencia Federal de Protección Ambiental de Estados Unidos (USEPA) a enmendar los estatutos relacionados con la calidad de agua potable para incluir un nivel máximo de concentración del total de trihalometanos (TTHMs) de 100 μmol/L (ppb). En Puerto Rico, la presencia de trihalometanos, substancias potencialmente cancerígenas, en el agua potable ha causado consternación entre el público en general, la industria y las agencias del gobierno. Se requiere, por tanto, un mejor entendimiento de aquellas variables operacionales del proceso de cloración de agua potable que afectan la formación de los trihalometanos.

En este trabajo, se identificaron dichas variables usando aguas crudas de diferentes áreas geográficas de Puerto Rico. Las más significativas fueron: contenido total de carbono organico no-volátil (NVTOC), pH, razón de dosis de cloro aplicado por unidad de NVTOC y concentracion del ión
bromuro. Se hizo un diseño experimental factorial con el propósito de cuantificar el efecto de estas variables sobre la concentración del total de trihalometanos formados durante el proceso de cloración.

Se diseñó y construyó una planta piloto para filtrar y clorar las aguas crudas, con la cual se llevaron a cabo los experimentos. Se desarrollaron técnicas analíticas para analizar rutinariamente las aguas crudas para contenido de NVTOC e iones bromuro.

Se desarrolló un modelo de regresión, altamente significativo, que relaciona la concentración de THMs con las variables operacionales antes identificadas. Cloro residual, una medida de la efectividad del proceso de desinfección, también fue medido y correlacionado con las mismas variables. La combinación de las dos correlaciones desarrolladas provee una herramienta útil para la minimización de la formación de THMs durante el proceso de cloración mientras que, a la vez, se garantiza una desinfección adecuada.
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Factorial Experimental Design for the Determination of the Effects of Operational Variables on the Formation of THMs During Water Chlorination

Two-Level Fractional Designs for 4 Variables and 8 Runs, $2^{4-1}$ (IV)

Replicate with Center Pointers

Factors used in Experimental Design

Results of the Experimental Design

Applied Chlorine Dose, Residual Chlorine and Residual pH Measured

Parameter Estimates Trihalomethanes Formation Models #1 and #2

ANOVA for Trihalomethanes Formation Models #1 and #2

Correlation Coefficient and Standard Errors of the Estimate for TTHM Formation Models #1 and #2

Parameter Estimates for Model #3 Describing Trihalomethanes Formation (95% Confidence Limits)
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I. Introduction

In 1974, trihalomethanes (chloroform, bromoform, bromodichloromethane, and dibromochloromethane) were discovered to be formed during the disinfection step of drinking water if free chlorine was the disinfectant. This led USEPA (United States Environmental Protection Agency) to amend the National Interim Primary Drinking Water Regulations to include a maximum contaminant level of 100 µg/L (ppb) for total trihalomethanes (TTHMs) in water.

In Puerto Rico, the presence of trihalomethanes in drinking water is a matter of serious concern for the general public, industry and government agencies. Recently, PRASA (Puerto Rico Aqueducts and Sewer Authority), has implemented some changes in their drinking water chlorination procedures in an effort to reduce the formation of THMs to levels within the federal regulations. Their efforts have been partially successful, although recent outbreaks of gastroenteritis in various parts of the Island seem to point out the apparent dichotomy between THMs formation reduction and proper disinfection practices.
A better understanding is needed of the chlorination parameters which affect the formation of trihalomethanes. Public health as well as industrial concerns could benefit substantially through the application of this understanding to the delivery of a drinking water which is safe, both from the chemical and bacteriological stand points.

In this work, we identified those operational variables involved in the chlorination of drinking waters which influence the formation of THMs, using raw waters from different geographical areas of Puerto Rico. A factorial experiment was carefully designed with the purpose of ascertaining the effect of those variables on total trihalomethanes formed during the chlorination process.

Pilot plant water filtration and chlorination facilities were designed and built in order to implement our multivariate analysis of the process. Analytical facilities were developed to routinely analyze water for THMs precursors, partially identified as humic and fulvic acids (characterized in terms of non-volatile total carbon, NVTOC) and bromide ion (Br⁻).
A highly significant regression model was developed relating TTHMs formation to the operational variables of the chlorination process. Residual chlorine, a measure of disinfection effectiveness, was also measured and correlated to the same variables. The two correlations developed provide a useful tool for minimization of THMs formation while guaranteeing proper disinfection.
II. Literature Review

Since the discovery in 1974 that small amounts of haloforms are produced as side reaction products during chlorination of natural colored waters\textsuperscript{1}, investigations have been carried out to find suitable technical conditions that would minimize haloform concentrations in the final product by reducing the precursors content before chlorination.

In the last few years, numerous researchers have studied the formation of THMs\textsuperscript{2}, and a great number of organic compounds that are possible precursors of importance to this process, have been identified. Two classes of compounds which have been considered as possible haloform precursors are humic materials\textsuperscript{3} and low molecular weight methyl ketone\textsuperscript{4}. Rook\textsuperscript{3} showed that m-dihydroxy aromatic compounds, common building blocks of humic materials, produce high levels of CHCl\textsubscript{3} during chlorination. Since they are present at high concentrations in most surface waters, there can be little doubt that humic substances are important precursors. The importance of methyl ketone as a haloform precursor is more speculative. Acetone\textsuperscript{5} and trichloroacetone\textsuperscript{6}, potential haloform precursors, have been also found in natural water.
Other studies\(^7\) have recognized bromide as an important precursor in the formation of THMs. In the presence of chlorine, bromide is oxidized to intermediates (likely \(\text{Br}_2\), \(\text{HOBr}\), and \(\text{OBr}^-\), with some \(\text{BrCl}\) and \(\text{BrCl}_3\))\(^8\), which apparently participate in the halogenation step of the THM reaction sequence much more effectively than does chlorine. This effect was noted by Kleopfer\(^9\) and has also been observed by others\(^10,11\). All of these researchers have observed that the presence of bromide increases the yield of THMs for a given chlorine dose. However, other researchers\(^2\) have found the opposite. Figure \#1 illustrates this phenomena. Note that as bromide concentration increases, \(\text{CHCl}_3\) formation decreases hence TTHM decreases.

The haloform reaction is extremely sensitive to a great number of physicochemical parameters. The formation of trihalomethanes is a function of temperature, pH, and chlorine concentration; ammonia and halides in treated water also have a significant effect on the quantity and the nature of the volatile organohalogenated products formed. In most cases, chloroform (\(\text{CHCl}_3\)), dichlorobromomethane (\(\text{CHBrCl}_2\)), dibromochloromethane (\(\text{CHBr}_2\text{Cl}\)), and bromoform (\(\text{CHBr}_3\)) are formed during chlorination\(^4\); iodinated compounds are not often observed.
Reactive residues: 55 µg/L; N-NH₄⁺: 0.1 mg/L.
Molar Ratio CLN: 12.5, 30 min; 18°C

Figure #1: Effect of Bromide Concentration on Trihalomethane Production (Ref. 2)
Chlorine is added to the drinking water primarily to prevent the spread of the water borne diseases such as hepatitis, poliomyelitis, typhoid and cholera\textsuperscript{12}. The reaction of chlorine (gas) in water can be described by the following chemical equations:

\[ \text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{H}^+ + \text{Cl}^- \]

\[ \text{HOCl} = \text{H}^+ + \text{OCl}^- \]

Hypochlorous acid (HOCl) is generally regarded as the active species which inactivates the microorganisms. The hydrolysis of HOCl is very fast\textsuperscript{13}. HOCl reacts with other water borne contaminants also. Because chlorine hardly exists as Cl\textsubscript{2} in water, the term aqueous chlorine has been coined to indicate HOCl, OCl\textsuperscript{-}, and other species such as NH\textsubscript{2}Cl, NHCl\textsubscript{2}. At pH 7.5 the activities of HOCl and OCl\textsuperscript{-} are approximately equal (see Figure #2). Below this pH, HOCl predominates and above pH 7.5 OCl\textsuperscript{-} predominates. This phenomenon is very important in disinfection chemistry because, generally, HOCl is about 80 percent more effective in killing bacteria than OCl\textsuperscript{-}. 
Figure #2: Calculated Fraction of Free Chlorine Species in Aqueous Solution (Ref. 13)
A variety of factors influence the THM formation reaction, including precursor type, precursor concentration (expressed as non-volatile total organic carbon [NVTOC]), chlorine (Cl₂) dosage (expressed as the ratio of Cl₂ to NVTOC [Cl₂/NVTOC]), temperature, pH, halogen ion (bromide or iodide) concentration, and time. These factors can affect the total yield of THMs as well as the rate at which THMs are formed. The effects of these factors have been discussed in the literature.

Two general strategies have been used in developing models for THMs formation: multiple linear regression model with logarithmic transformations of both dependent and independent variables, referred to as the log-log model, and multiple nonlinear regression models. Both models, in their original form, take the form of multiple parameter additive models, although retransformation of the log-log model back into its original variables yields a multiparameter power function.

Trussell proposed a differential rate expression relating the rate of THMs production to chlorine residual to the first power and the precursor concentration to the m\textsuperscript{th} power. A good fit of experimental data was observed when
NVTOC was used as a surrogate parameter for the precursor concentration and m was assumed to be 3.
III. Experimental Procedure

III.A. Water Filtration and Chlorination Facilities

A chlorination pilot plant was designed and built for this project. This equipment is capable of processing up to 55 gallons of raw water per batch. The chlorination plant consists of three primary units: a coagulation tank, a sand filtration column and a chlorination tank with a feeder for the sand filter column.

Basically, the plant operates as follows: raw water from a source is pumped into the coagulation tank, where solutions of alum and sodium hydroxide are fed from stock solutions prepared previously. The sodium hydroxide solution is used for pH adjustment control. The concentration of each solution prepared is manipulated independently, according to the desired operating conditions. The alum solution is a coagulant agent to help in the flocculation of particulate suspended matter contained in the raw water. The coagulation tank is fitted with a blade agitation assembly. The clean water overflows the tank and flows through the sand filtering column, from where it is withdrawn as the final product to be chlorinated.
III.B. Analytical Techniques

THMs concentrations were analyzed by means of chromatographic techniques. The system uses (see Figure #3) the purge and trap method for sample concentration (Perkin Elmer LSC-2 liquid sample concentrator), a temperature programmed gas chromatographic separation, and detection by an electrolytic conductivity detector (Perkin-Elmer model 700A). The purge and trap method extracts THMs from the aqueous sample by bubbling of an inert gas. The THMs are then carried away with the purge gas and collected on a short trapping column that is kept at ambient temperature. After the aqueous sample has been thoroughly purged, the trapped components are thermally desorbed and backflushed onto the analytical column. The precision of this method has been certified by several investigators\textsuperscript{17}.

The method is applicable in the determination of chloroform, dichlorobromomethane, dibromochloromethane, and bromoform in drinking water or raw source water. The concentration of these four compounds may be added to determine total trihalomethanes (TTHM). The method can be used over a concentration range of approximately 0.1 to 1500 micrograms per liter.
Humic and fulvic acids were determined as non-volatile total organic carbon (NVTOC). The carbon analyzer used (O.I. 524C) consists of an ampule analyzing unit and a purging and sealing unit (see Figure #4).

The sample is acidified, purged to remove inorganic carbon, and oxidized with persulfate in an autoclave at a temperature of 250 °F and 15 psig of pressure. The resultant carbon dioxide (CO₂) is measured by non-dispersive infrared spectrometry.

Bromide concentrations were analyzed by means of a spectrophotometric standard method\textsuperscript{18}. A Beckman 25 UV/VIS spectrophotometer at a fixed wavelength of 590 nm and a 2 cm cell light path was used.

Total residual chlorine was determined by using an electrode (Orion-Model 97-70) and the laboratory meter (Orion-Model 407A). The procedure requires the use of a standard solution of 1 ppm residual chlorine for meter calibration. This allows measurement of samples with total residual chlorine concentrations between 0.2-20 ppm.
To ensure proper disinfection results the chlorinated water samples were analyzed for total and fecal coliforms, using the standard Total Coliform Multiple-Tube Tests and Fecal Coliform MPN procedures\textsuperscript{18}

III.C. Experimental Design

Laboratory data were obtained to ascertain the effects on the formation of THMs of several operational variables in the water chlorination process. The variables considered were:

(1) precursors concentration in the raw water (humic and fulvic acids, characterized as NVTOC),

(2) pH,

(3) bromide ion (Br\textsuperscript{-}) concentration, and,

(4) applied chlorine dose.

Recent works\textsuperscript{16,19,20,21,22} have demonstrated that these are the significant variables involved. These authors also emphasize that the models postulated so far are very site-specific. They must be calibrated and validated using local data. However, there is widespread agreement that the variables mentioned above provide an adequate framework for generalized modelling efforts of this complex reaction system.
Various raw water supplies for the San Juan metropolitan area, Ponce and Mayagüez were characterized (pH, bromide ion concentration and NVTOC content). A spectrophotometric standard method with cell path of 2 centimeters was used for bromide analysis. Humic and fulvic acids were analyzed using a total organic carbon analyzer (NVTOC). In this technique, infrared spectroscopy is used as a detector of CO₂.

For each water supply, experiments were conducted at different pH levels and chlorine doses. Two pH levels were considered: ambient ±1.5 units. Two levels of chlorine doses were included, in terms of the ratio of Cl₂ to non-volatile total organic carbon (NVTOC) in the raw water: 1.0 and 3.0 (mass basis). Table I summarizes the 2⁴ experimental design proposed. Table IIA summarizes a fractional factorial design as replicate and Table IIB summarizes four replicates with center points. Samples of the chlorinated water were taken four days after chlorination (characteristic of detention times in large water distribution systems), and analyzed for THMs using the purge and trap method, adopted as a standard method by USEPA. They were also analyzed for chlorine residual and bacteriological activity to ensure proper disinfection results were achieved.
### Table I: Factorial Experimental Design for the Determination of the Effects of Operational Variables on the Formation of THMs During Water Chlorination

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<th>Cl&lt;sub&gt;2&lt;/sub&gt;/NVTOC&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>+</td>
</tr>
</tbody>
</table>

**Note:**

+ High level
- Low level

<sup>a</sup> Non volatile total organic carbon concentration in the raw water, mg/L.

<sup>b</sup> Applied chlorine dose, mass of chlorine per unit mass of NVTOC.

<sup>c</sup> Bromide ion concentration in the water, mg/L.
Table IIA. Two-Level Fractional Designs for 4 Variables and 8 Runs (Resolution IV Design, $2^{4-1}(IV)$).²⁴

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>NVTOCᵃ</th>
<th>pH</th>
<th>Cl₂/NVTOCᵇ</th>
<th>Br⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Table IIB. Replicate with center points

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>NVTOCᵃ</th>
<th>pH</th>
<th>Cl₂/NVTOCᵇ</th>
<th>Br⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note:
+ High level
- Low level
0 Mean level

ᵃ Non volatile total organic carbon concentration in the raw water, mg/L.

ᵇ Applied chlorine dose, mass of chlorine per unit mass of NVTOC.

ᶜ Bromide ion concentration in the water, mg/L.
The data obtained were analyzed by multiple regression analysis to obtain a correlation between TTHM formation and: precursors concentrations (bromide and humic and fulvic acids), pH, and Cl₂/NVTOC. Another correlation was obtained between residual chlorine and: NVTOC, pH, applied chlorine dose, and bromide.
IV. Results

IV.A. Data Obtained

Information obtained is based on the analytical techniques mentioned earlier. Further information (specific results, procedure details, calibration curves) can be found on Appendix A. Prominent information is provided here.

The factors identified as important in the formation of THMs were coded as described in Table III.

Table III. Factors Used in Experimental Design

<table>
<thead>
<tr>
<th>Code</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$X_1$ [NVTOC], mg/L</td>
<td>3.44</td>
</tr>
<tr>
<td>$X_2$ pH</td>
<td>amb.* - 1.5</td>
</tr>
<tr>
<td>$X_3$ [Cl$_2$]/[NVTOC]</td>
<td>1</td>
</tr>
<tr>
<td>$X_4$ [Bromide]</td>
<td>amb. + 0.2</td>
</tr>
</tbody>
</table>

* amb. = ambient value
- low level
+ high level
0 mean level
Factor $X_1$ refers to non-volatile total organic carbon concentration. For Mayagüez its value was 3.44 mg/L; for San Juan it was 4.93 mg/L (see Appendix A). Factor $X_2$ refers to pH of reaction. For Mayagüez, ambient water pH was 7.5; for San Juan it was 7.2. Factor $X_3$ refers to the ratio between applied chlorine dose (mg/L) and [NVTOC]. Factor $X_4$ refers to bromide concentration in the raw water. For Mayagüez, ambient water concentration was 0.26 mg/L; for San Juan it was below the detection limit of the technique used.

A summary of the experimental data obtained for the four factors described above can be found in the Table IV. The 28 runs were randomized before the experiments were performed. In that table the measurement for TTHM formation in run # 20 was missing.

Other experimental data obtained were residual chlorine and residual pH and they are summarized in the Table V. These data were measured 96 hours after chlorination.
Table IV. Results of the Experimental Design

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$X_3$</th>
<th>$X_4$</th>
<th>$Y$</th>
<th>Order of runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.44</td>
<td>6.0</td>
<td>1.0</td>
<td>0.46</td>
<td>0.503</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>4.93</td>
<td>5.7</td>
<td>1.0</td>
<td>0.20</td>
<td>0.677</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>3.44</td>
<td>9.0</td>
<td>1.0</td>
<td>0.46</td>
<td>0.906</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>4.93</td>
<td>8.7</td>
<td>1.0</td>
<td>0.20</td>
<td>1.301</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>3.44</td>
<td>6.0</td>
<td>3.0</td>
<td>0.46</td>
<td>0.601</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>4.93</td>
<td>5.7</td>
<td>3.0</td>
<td>0.20</td>
<td>0.753</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>3.44</td>
<td>9.0</td>
<td>3.0</td>
<td>0.46</td>
<td>1.718</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>4.93</td>
<td>8.7</td>
<td>3.0</td>
<td>0.20</td>
<td>1.667</td>
<td>17</td>
</tr>
<tr>
<td>9</td>
<td>3.44</td>
<td>6.0</td>
<td>1.0</td>
<td>0.66</td>
<td>0.523</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>4.93</td>
<td>5.7</td>
<td>1.0</td>
<td>0.40</td>
<td>0.780</td>
<td>24</td>
</tr>
<tr>
<td>11</td>
<td>3.44</td>
<td>9.0</td>
<td>1.0</td>
<td>0.66</td>
<td>0.905</td>
<td>5</td>
</tr>
<tr>
<td>12</td>
<td>4.93</td>
<td>8.7</td>
<td>1.0</td>
<td>0.40</td>
<td>1.482</td>
<td>23</td>
</tr>
<tr>
<td>13</td>
<td>3.44</td>
<td>6.0</td>
<td>3.0</td>
<td>0.66</td>
<td>0.552</td>
<td>2</td>
</tr>
<tr>
<td>14</td>
<td>4.93</td>
<td>5.7</td>
<td>3.0</td>
<td>0.40</td>
<td>0.876</td>
<td>25</td>
</tr>
<tr>
<td>15</td>
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<td>9.0</td>
<td>3.0</td>
<td>0.66</td>
<td>1.382</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>4.93</td>
<td>8.7</td>
<td>3.0</td>
<td>0.40</td>
<td>2.027</td>
<td>27</td>
</tr>
<tr>
<td>17</td>
<td>3.44</td>
<td>6.0</td>
<td>1.0</td>
<td>0.46</td>
<td>0.509</td>
<td>3</td>
</tr>
<tr>
<td>18</td>
<td>4.93</td>
<td>5.7</td>
<td>1.0</td>
<td>0.40</td>
<td>0.715</td>
<td>19</td>
</tr>
<tr>
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<td>9.0</td>
<td>1.0</td>
<td>0.66</td>
<td>0.886</td>
<td>12</td>
</tr>
<tr>
<td>20</td>
<td>4.93</td>
<td>8.7</td>
<td>1.0</td>
<td>0.20</td>
<td>*</td>
<td>15</td>
</tr>
<tr>
<td>21</td>
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<td>3.0</td>
<td>0.66</td>
<td>0.718</td>
<td>13</td>
</tr>
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<td>5.7</td>
<td>3.0</td>
<td>0.20</td>
<td>0.974</td>
<td>16</td>
</tr>
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<td>3.0</td>
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<td>1.796</td>
<td>11</td>
</tr>
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<td>8.7</td>
<td>3.0</td>
<td>0.40</td>
<td>1.899</td>
<td>26</td>
</tr>
<tr>
<td>25</td>
<td>3.44</td>
<td>7.5</td>
<td>1.5</td>
<td>0.56</td>
<td>0.920</td>
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<td>0.56</td>
<td>0.943</td>
<td>14</td>
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<td>4.93</td>
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<td>0.30</td>
<td>1.241</td>
<td>21</td>
</tr>
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<td>28</td>
<td>4.93</td>
<td>7.2</td>
<td>1.5</td>
<td>0.30</td>
<td>1.115</td>
<td>28</td>
</tr>
</tbody>
</table>

Note:

- $Y$: TTHMs, μmol/L
- $X_1$: [NVTOC], mg/L
- $X_2$: pH,
- $X_3$: $[\text{Cl}_2]/[\text{NVTOC}], \text{ (mg/L)/(mg/L)}$
- $X_4$: [Br$^-$], mg/L

* Missing data, experiment # 20
a Randomization of order of experimentation
Table V. Applied Chlorine Dose, Residual Chlorine and Residual pH Measured

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Applied Cl₂ Dose (ppm)</th>
<th>Residual Chlorine (ppm)</th>
<th>Residual pH*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.44</td>
<td>0.87</td>
<td>6.45</td>
</tr>
<tr>
<td>2</td>
<td>4.93</td>
<td>1.28</td>
<td>6.10</td>
</tr>
<tr>
<td>3</td>
<td>3.44</td>
<td>0.21</td>
<td>8.65</td>
</tr>
<tr>
<td>4</td>
<td>4.93</td>
<td>0.87</td>
<td>8.35</td>
</tr>
<tr>
<td>5</td>
<td>10.32</td>
<td>6.20</td>
<td>6.35</td>
</tr>
<tr>
<td>6</td>
<td>14.79</td>
<td>12.60</td>
<td>5.95</td>
</tr>
<tr>
<td>7</td>
<td>10.32</td>
<td>7.00</td>
<td>8.60</td>
</tr>
<tr>
<td>8</td>
<td>14.79</td>
<td>10.20</td>
<td>5.10</td>
</tr>
<tr>
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<td>3.44</td>
<td>0.83</td>
<td>6.20</td>
</tr>
<tr>
<td>10</td>
<td>4.93</td>
<td>1.20</td>
<td>5.90</td>
</tr>
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<td>3.44</td>
<td>0.40</td>
<td>8.60</td>
</tr>
<tr>
<td>12</td>
<td>4.93</td>
<td>0.70</td>
<td>8.50</td>
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<td>10.32</td>
<td>7.58</td>
<td>6.35</td>
</tr>
<tr>
<td>14</td>
<td>14.79</td>
<td>10.80</td>
<td>5.95</td>
</tr>
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<td>15</td>
<td>10.32</td>
<td>7.10</td>
<td>9.10</td>
</tr>
<tr>
<td>16</td>
<td>14.79</td>
<td>8.10</td>
<td>8.50</td>
</tr>
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<td>3.44</td>
<td>0.75</td>
<td>6.25</td>
</tr>
<tr>
<td>18</td>
<td>4.93</td>
<td>1.63</td>
<td>6.00</td>
</tr>
<tr>
<td>19</td>
<td>3.44</td>
<td>0.12</td>
<td>8.55</td>
</tr>
<tr>
<td>20</td>
<td>4.93</td>
<td>1.02</td>
<td>8.45</td>
</tr>
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<td>21</td>
<td>10.32</td>
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</tr>
<tr>
<td>22</td>
<td>14.79</td>
<td>9.80</td>
<td>6.35</td>
</tr>
<tr>
<td>23</td>
<td>10.32</td>
<td>5.30</td>
<td>8.55</td>
</tr>
<tr>
<td>24</td>
<td>14.79</td>
<td>7.00</td>
<td>8.45</td>
</tr>
<tr>
<td>25</td>
<td>5.16</td>
<td>0.92</td>
<td>7.45</td>
</tr>
<tr>
<td>26</td>
<td>5.16</td>
<td>0.79</td>
<td>7.20</td>
</tr>
<tr>
<td>27</td>
<td>7.395</td>
<td>2.55</td>
<td>7.40</td>
</tr>
<tr>
<td>28</td>
<td>7.395</td>
<td>2.80</td>
<td>7.00</td>
</tr>
</tbody>
</table>

* Residuals were measured 96 hours after chlorination
IV.B. Regression Models

A computer program was used (see Appendix C) for the development of two regression models: one model relating THMs formation to operational variables, and the other relating residual chlorine to the same operational variables.

IV.B.1 Model to Describe Trihalomethanes Formation

Various models were tested for this purpose. The first one, named Model #1, was of the form:

\[ Y = b_{01} + b_{11}X_1 + b_{21}X_2 + b_{31}X_3 + b_{41}X_4, \]

where \( b_{ij} \) is the coefficient of variable \( i \) in model \( j \).

Another model tested, named Model #2, was the log-log model, which yields a multiparameter power function of the form:

\[ Y = b_{02} X_1^{b_{12}} X_2^{b_{22}} X_3^{b_{32}} X_4^{b_{42}} \]
Using the program in Appendix C, the best parameter estimates were obtained for these two models. The results are presented in Table VI. The analysis of variance (ANOVA) for these models is shown in Table VII. Correlation coefficients and standard errors of the estimate are shown in Table VIII.

Table VI: Parameter Estimates for Trihalomethanes Formation Models #1 and #2

<table>
<thead>
<tr>
<th>Variable Number(i)</th>
<th>Model #1a</th>
<th>Model #2b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b_{i1}$</td>
<td>S.E</td>
</tr>
<tr>
<td>0</td>
<td>-2.14590</td>
<td>0.48264</td>
</tr>
<tr>
<td>1</td>
<td>0.24031</td>
<td>0.07394</td>
</tr>
<tr>
<td>2</td>
<td>0.25625</td>
<td>0.02352</td>
</tr>
<tr>
<td>3</td>
<td>0.17541</td>
<td>0.03453</td>
</tr>
<tr>
<td>4</td>
<td>-0.03965</td>
<td>0.35284</td>
</tr>
</tbody>
</table>

\[ Y = \sum_{i=1}^{n} b_{i1} X_i \]

\[ Y = b_{i2} \prod_{i=1}^{4} b_{i2} X_i \]

\[ t_c = t(22, 0.05) = 2.074 \]
Table VII: ANOVA For Trihalomethanes Formation Models #1 and #2

<table>
<thead>
<tr>
<th></th>
<th>Model #1</th>
<th>Model #2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS</td>
<td>F-test</td>
</tr>
<tr>
<td>Total(corr.)</td>
<td>35.24168</td>
<td></td>
</tr>
<tr>
<td>Regression</td>
<td>34.80085</td>
<td>347.36&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Residual</td>
<td>0.44085</td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>0.38088</td>
<td>4.40&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pure error</td>
<td>0.05995</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> F(5,21,0.95) = 2.68  
<sup>b</sup> F(13,9,0.95) = 3.05

Table VIII: Correlation Coefficients and Standard Errors of the Estimate for TTHM Formation Models #1 and #2

<table>
<thead>
<tr>
<th></th>
<th>Model #1</th>
<th>Model #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation coefficient (R&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>0.8762</td>
<td>0.9189</td>
</tr>
<tr>
<td>Standard error (μmol/L)</td>
<td>0.1416</td>
<td>0.1748</td>
</tr>
</tbody>
</table>

After testing many additional models, and performing similar statistical tests, the model chosen, named Model #3, was of the form:

\[ Y = b_{03} + b_{13}X_1 + b_{23}\ln(X_2) + b_{33}X_3 + b_{43}/X_4 + b_{53}X_5, \]

where \( X_5 = X_2X_3. \)

The best parameter values with 95% confidence limits were obtained and are presented in Table IX.
Table IX: Parameters Estimates for Model #3 Describing Trihalomethanes Formation (95% Confidence Limits)

<table>
<thead>
<tr>
<th></th>
<th>Estimate</th>
<th>Standard error</th>
<th>Lower limit</th>
<th>Upper limit</th>
<th>t-value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>b_03</td>
<td>-1.745700</td>
<td>0.53703</td>
<td>-2.86270</td>
<td>-0.62868</td>
<td>-3.251</td>
</tr>
<tr>
<td>b_13</td>
<td>0.279950</td>
<td>0.04245</td>
<td>0.19165</td>
<td>0.36825</td>
<td>6.595</td>
</tr>
<tr>
<td>b_23</td>
<td>0.694790</td>
<td>0.25433</td>
<td>0.16578</td>
<td>1.22380</td>
<td>2.732</td>
</tr>
<tr>
<td>b_33</td>
<td>-0.390370</td>
<td>0.11566</td>
<td>-0.63094</td>
<td>-0.14980</td>
<td>-3.375</td>
</tr>
<tr>
<td>b_43</td>
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<td>0.02630</td>
<td>-0.08922</td>
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<td>-1.312</td>
</tr>
<tr>
<td>b_53</td>
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<td>0.01548</td>
<td>0.04593</td>
<td>0.11030</td>
<td>5.064</td>
</tr>
</tbody>
</table>

* tc = t(21, 0.05) = 2.080

The analysis of variance (ANOVA) for this model can be found in Table B.1 and the corresponding data can be found in Table B.3, both from Appendix B. They are summarized in Table X.

Table X: ANOVA for Trihalomethanes Formation Model #3

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>Calc. F</th>
<th>F_{0.95}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total(corrected)</td>
<td>26</td>
<td>5.43427</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regression</td>
<td>5</td>
<td>5.14992</td>
<td>1.029984</td>
<td>76.09</td>
<td>2.68</td>
</tr>
<tr>
<td>Residual</td>
<td>21</td>
<td>0.28427</td>
<td>0.013537</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>12</td>
<td>0.22432</td>
<td>0.018693</td>
<td>2.81</td>
<td>3.07</td>
</tr>
<tr>
<td>Pure error</td>
<td>9</td>
<td>0.05995</td>
<td>0.006661</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The lack of fit is not statistically significant since 2.81 < F(12, 9, 0.95) = 3.07, while the model is greatly significant since F(5, 21, 0.99) = 4.04 << 76.09, and 99% of
the variation about the mean is explained by the regression.

The correlation coefficient ($R^2$) was calculated equal to 0.9477. The standard error of the predicted values was found to be 0.12 μmol/L. Observed values versus predicted values are shown in Fig. 5.

IV.B.2 Model to Describe the Residual Chlorine.

The model chosen to describe residual chlorine is of the form

$$Y_2 = b_{14}X_1 + b_{44}/X_4 + b_{64}X_6 + b_{74}X_7,$$

where $Y_2$ is residual chlorine in ppm, $X_6$ is the applied chlorine dose, in ppm, and $X_7 = X_2X_6$.

Using the program in Appendix C the best parameter values with 95% confidence limits were obtained. They were estimated by linearization for the individual parameter. The results are presented in Table XI.
Figure #5: Plot of TTHM Concentration (μmol/L): Observed vs Predicted Values
Table XI: Parameters Estimates for the Model Describing Residual Chlorine (95% Confidence Limits).

<table>
<thead>
<tr>
<th>Estimate</th>
<th>Standard error</th>
<th>Lower limit</th>
<th>Upper limit</th>
<th>t-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>b_{14}</td>
<td>-0.966360</td>
<td>0.14477</td>
<td>-1.265900</td>
<td>-0.66683</td>
</tr>
<tr>
<td>b_{24}</td>
<td>0.375150</td>
<td>0.18364</td>
<td>-0.005443</td>
<td>0.75574</td>
</tr>
<tr>
<td>b_{64}</td>
<td>1.150600</td>
<td>0.10164</td>
<td>0.940310</td>
<td>1.36090</td>
</tr>
<tr>
<td>b_{74}</td>
<td>-0.037094</td>
<td>0.01247</td>
<td>-0.062892</td>
<td>-0.01129</td>
</tr>
</tbody>
</table>

* tc = t(23, 0.05) = 2.069

The analysis of variance for this model can be found in Table B.2 from Appendix B and the corresponding data can be found in Table B.4, also from Appendix B. They are summarized in Table XII.

Table XII: ANOVA for Residual Chlorine Model

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>Calc. F</th>
<th>F_{0.95}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total(corrected)</td>
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<td>868.2109</td>
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<tr>
<td>Regression</td>
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<td>850.1203</td>
<td>212.53</td>
<td>270.22</td>
<td>2.80</td>
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<tr>
<td>Residual</td>
<td>23</td>
<td>18.0905</td>
<td>0.7865</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>14</td>
<td>9.6735</td>
<td>0.6910</td>
<td>0.740</td>
<td>3.03</td>
</tr>
<tr>
<td>Pure error</td>
<td>9</td>
<td>8.4170</td>
<td>0.9352</td>
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<td></td>
</tr>
</tbody>
</table>

The lack of fit is not statistically significant since 0.74 < F(12, 9, 0.95) = 3.03, while the model is greatly significant since F(5, 21, 0.99) = 4.26 << 270.22 and 99% of
the variation about the mean is explained by the regression.

The correlation coefficient ($R^2$) was calculated equal to 0.9792. The standard error of the predicted values was found to be 0.89 ppm. Observed values versus predicted values are shown in Fig. 6.
Figure #6: Plot of Residual Chlorine (ppm), Observed vs Predicted Values
TTHMs were performed in a government laboratory facility where, usually, samples analyzed do not exceed significantly the 100 ppb standard, unlike our samples.

The regression model was also tested from the point of view of residuals analysis (observed minus predicted values). Figure B.1 is a normal probability plot of the residuals, and it shows that they follow, almost perfectly, a normal distribution. This provides further evidence that the regression model developed describes appropriately the observed data.

Table IX presents estimates of parameters for the chosen TTHMs regression model, with their corresponding 95% confidence limits. All parameters, except \( b_{43} \) which relates to the effect of bromide concentration, show relatively narrow 95% confidence intervals and are significantly different from zero. For the case of \( b_{43} \), statistically speaking, it is not significantly different from zero. However, the data shows a strong effect of bromide concentration on TTHMs formation. This discrepancy could be due to the fact that the two levels chosen for bromide analysis in our experimental design (0.2 and 0.66 ppm) were not sufficiently different from each other to ascertain the true effect of bromide concentration on TTHMs formation.
According to the model developed, TTHMs formation varies with the reciprocal of bromide ion concentration, with a negative coefficient. Therefore, TTHMs formation increases as bromide concentration increases. This behavior is to be expected since three of the TTHMs contain bromide. Because of this type of functionality, TTHMs formation is highly sensitive to bromide concentration changes at very low values, but almost insensitive to it at the higher concentration levels used in this work. Although it is not recommended to extrapolate when using a regression model such as the one developed for predictive purposes, we explored its ability to predict TTHMs formation when no chlorine is added at low bromide concentrations. For a pH of 7.0 and NVTOC of 3.5 ppm, the model predicts no TTHMs formation below a bromide content of 0.06 ppm (obviously, only positive values of TTHMs are considered). This concentration is below the level of detection of the technique used for bromide analysis.

To obtain a better understanding of the effect of the operational variables on TTHMs concentrations predicted by the model chosen, Figures 7, 8, 9 and 10 were generated. TTHMs formation increases at higher pH levels. Extrapolating the curves it was found that the model predicts no formation of THMs for a pH value under 2.84. This is in excellent agreement with a value of 2.8 reported in the literature\textsuperscript{16,21}. 
Figure #7: Plot of TTHM vs pH
(Br⁻ = 0.3 ppm, NVTOC = 3.6 ppm)
Figure #8: Plot of TTHM vs pH
\( (\text{Br}^- = 0.3 \text{ ppm, NVTOC} = 4.9 \text{ ppm}) \)
Figure #9: Plot of TTHM vs pH
\( \text{Br}^- = 0.65 \text{ ppm, } \text{NVTOC} = 3.60 \text{ ppm} \)
Figure #10: Plot of TTHM vs pH
(\(Br^- = 0.65\ \text{ppm},\ \text{NVTOC} = 4.90\ \text{ppm}\))
This behavior is to be expected, since, as shown in Fig. #2, below this pH most of the chlorine is in the gaseous state, and there is almost no HOCl' or OCl', the active species in solution.

The ability of the model to predict THMs formation at low NVTOC levels was also explored. Since NVTOC is used as a surrogate parameter for THMs precursors concentration, it was expected that the model would predict no formation of THMs at very low levels of this parameter. However, by extrapolation it was found that no formation was predicted for NVTOC concentrations below 1.4 ppm. Since the NVTOC analysis was performed on the raw water, previous to clarification, this behavior seems to indicate that a significant reduction of available NVTOC was accomplished through the clarification process. This phenomenon is presently being explored in the literature\textsuperscript{25,26}.

Residual chlorine data was also obtained and a regression model developed relating it to NVTOC, applied chlorine dose, pH, and bromide. As shown in Table XII, the regression is highly significant (higher than 99%). Lack of fit is not significant. Observed minus predicted values of residual chlorine are plotted in Figure B.2, a normal probability plot. Again, this analysis provides further
evidence that the regression model developed is a good one.

The two regression models developed in this work can be used simultaneously to optimize the process of chlorination of drinking waters with the objective of minimizing the formation of TTHMs, while maintaining proper disinfection. It has been established previously that a residual chlorine of between 0.2 and 0.8 ppm will ensure proper disinfection. (It should be pointed out that in all of the experimental runs residual chlorine values in this range, and higher, were observed. All samples in this range were analyzed for total and fecal coliform and no bacteriological activity could be detected). For a given set of characteristics of the water to be chlorinated (NVTOC, pH, and bromide concentration) the second model developed in this work can be used to determine the required chlorine dose to maintain a residual chlorine in the desired range. The first model can then be used to predict the resulting TTHMs concentration. For example, to maintain a residual level of 0.3 ppm in a water with a pH of 7.0, NVTOC concentration of 3.5 ppm, and Br⁻ concentration of 0.3 ppm, the second model predicts that the required chlorine dose is 2.73 ppm. This would result in a ratio of Cl₂/NVTOC of 0.780. Under these conditions, the first model predicts a resulting TTHMs of 0.593 μmol/L. To convert this result to ppb an average
molecular weight for the TTHMs mixtures resulting from all our experimental runs was calculated. The result was 182 kgs/kmole. Therefore, the predicted TTHMs concentration, on a mass basis, is 107.94 ppb.
V. Conclusions and Recommendations

1. The formation of TTHMs during the chlorination of drinking water was described quantitatively in terms of the following operational variables: pH, NVTOC and bromide content of the raw water, and the ratio of applied chlorine dose to NVTOC.

2. Residual chlorine, measured 96 hours after chlorination, was also described quantitatively in terms of the following variables: pH, NVTOC, and bromide content of the raw water, and applied chlorine dose.

3. Both regression models developed were highly significant from the statistical point of view.

4. They can be used simultaneously to optimize the water chlorination process with the objective of minimizing TTHMs formation while maintaining proper disinfection of the finished product.
Bibliography


Appendix A

Experimental Procedure Details
A.1 Detailed Experimental Procedure

1. Sampling for analysis of NVTOC of different areas of Puerto Rico.
2. Selection of lowest and highest NVTOC concentration area.
3. Measurement of pH and bromide concentration of both areas.
4. Filtration and clarification of each water sample using pilot plant designed.
5. Bromination dose is added to each sample.
6. Chlorination dose is added to each sample.
7. Adjustment of pH is made.
8. Sample is allowed to stand on amber flasks during 96 hours (22 °C).
9. Samples are collected for TTHM analysis.
A.2 Analytical Techniques Details:

A.2.1 Non-Volatile Organic Carbon Analysis.

Procedure:
1. Add 0.2 grams granular potassium persulfate or 1.0 ml of a saturated (7 g/100 ml) potassium persulfate to each ampule.
2. Add sample (5 ml).
3. Add 0.2 ml of 10% phosphoric acid solution.
4. Add distilled water if necessary.
5. The ampules are ready to be purged of inorganic carbon and sealed.
6. The sealed ampules are sterilized for 45 min at 250 °F (15 psig) in a autoclave.
7. Measure the NVTOC of each sample by means of a non-dispersive infrared analyzer.
Preparation of standard carbon dioxide curve:

1. The following procedure is used in making the standard solution: take 2.126 grams of potassium biphthalate (KHP) and dilute to 1000 ml with distilled water in a volumetric flask. Take 12, 8, 6, 4, 2, 1 ml of the 1000 ppm solution and dilute volumetrically to a solution which has organic carbon concentration as KHP of 12, 8, 6, 4, 2, 1 ppm.

2. Calibration curves (Fig. A.1 and Fig. A.2) were prepared using the information from Table A.1 in which measurements of standard concentrations are presented.

<table>
<thead>
<tr>
<th>Standard Concentration X1, (ppm)</th>
<th>Integrator Area, Yc</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mayagüez</td>
<td>San Juan</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>10840</td>
<td>9518</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20481</td>
<td>18529</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>37214</td>
<td>35283</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>52341</td>
<td>48037</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>68675</td>
<td>64253</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>94472</td>
<td>89582</td>
<td></td>
</tr>
</tbody>
</table>
Figure A.1: Calibration Curve for NVTOC
From Mayaguez
Figure A.2: Calibration Curve for NVTOC from San Juan
Sample Concentration Measurement:

From results Table A.3 and Figure A.1 and Figure A.2 we can obtain the measured concentration for each sample. Corresponding blanks were prepared to correct each sample measurement (see Table A.2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Integrator Area</th>
<th>Concentration (ppm)</th>
<th>Concentration Corrected, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mayagüez</td>
<td>33639</td>
<td>3.58</td>
<td>3.44</td>
</tr>
<tr>
<td>Mayagüez (blank)</td>
<td>3166</td>
<td>0.14</td>
<td></td>
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<tr>
<td>San Juan</td>
<td>42580</td>
<td>5.08</td>
<td>4.93</td>
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<tr>
<td>San Juan (blank)</td>
<td>2655</td>
<td>0.15</td>
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</table>

Table A.3: Regression Model for Determination of NVTOC

<table>
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<tr>
<th>Parameter</th>
<th>Mayagüez</th>
<th>San Juan</th>
</tr>
</thead>
<tbody>
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<td>A</td>
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<td>1356.916</td>
</tr>
<tr>
<td>B</td>
<td>9367.047</td>
<td>8856.428</td>
</tr>
<tr>
<td>C</td>
<td>-136.731</td>
<td>-110.018</td>
</tr>
</tbody>
</table>

Coefficient correlation 0.9996 0.9987

Regression Model \( Y_c = A + B \times X_c + C \times X_c^2 \)
A.2.2 Bromide Concentration Measurement

This analysis was performed by using technique 405 described on Standard Methods for the Examination of Water and Wastewater, 16th Edition, pp. 278-279.

In the Table A.4 we have presented the data for the calibration curve (Fig. A.3). From this figure or through a regression model the concentration of the sample can be obtained (see Table A.5).

<table>
<thead>
<tr>
<th>Standard Concentration (ppm), Xb</th>
<th>Absorbance Measured Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>0.2</td>
<td>0.038</td>
</tr>
<tr>
<td>0.4</td>
<td>0.076</td>
</tr>
<tr>
<td>0.6</td>
<td>0.115</td>
</tr>
<tr>
<td>0.8</td>
<td>0.144</td>
</tr>
<tr>
<td>1.2</td>
<td>0.182</td>
</tr>
</tbody>
</table>

Regression Model : \( Yb = 0.181 \times Xb + 0.002 \)
Coefficient of correlation = 0.9985
Figure A.3: Calibration Curve for Bromide from Mayaguez
Table A.5: Bromide Concentration for Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance</th>
<th>Concentration, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mayagüez</td>
<td>0.049</td>
<td>0.26</td>
</tr>
<tr>
<td>San Juan</td>
<td>0.000</td>
<td>N.D*</td>
</tr>
</tbody>
</table>

* Not detected

A.2.3 pH Measurement

This analysis was performed by using a Sargent-Welch (model LS) pH meter, adjusted with two standard calibration solutions (pH = 4 and pH = 10).

A.2.4 Total Residual Chlorine Measurement

This analysis was performed by using a total residual chlorine electrode.

Procedure for samples between 0.2 and 20 ppm:

Standardizing solution (1 ppm):
1. Pipet 1 ml residual chlorine standard (100 ppm as Cl₂), 1 ml iodide reagent, and 1 ml
acid reagent into a 150 ml beaker. Use only 1 ml of each solution, and do not add water. Swirl for two minutes to allow complete reaction.

2. Add 99 ml distilled water and mix thoroughly.

3. Store this 1 ppm standardizing solution in the storage bottle for calibration. Prepare a solution every day.

Measurement using 407A meter:

1. Turn the function switch to X". Set the slope indicator dial to 100% slope. Turn the temperature compensator knob until white arrow points to 20 °C.

2. Place the electrode in the 1 ppm standardizing solution so that the reference element is submerged.

3. Turn the calibration control knob until its needle points to "1" (at the center of the red logarithmic scale).

4. Remove the electrode from the solution. Blot dry. Replace the cap back to its storage bottle.
5. Transfer a 100 ml sample to a 150 ml beaker. Add 1 ml each of iodide reagent and acid reagent. Mix thoroughly and let stand for about two minutes to allow complete reaction.

6. Place the electrode in the sample so that the reference element is submerged. The reading on the red logarithmic scale is equal to the sample total residual chlorine concentration.

7. Recalibrate every two hours by repeating steps 2-4 above.

A.2.5 TTHM measurement.

This analysis was performed by using method 502.1 prepared by the staff of research and development of EPA (EPA # 600/4-81-059). The results obtained can be found on table A.6 and correspond to the sum of chloroform, bromoform, dichlorobromomethane, and dibromochloromethane concentrations. In this table

\[ Y = \frac{y_1}{119.378} + \frac{y_2}{163.834} + \frac{y_3}{208.290} + \frac{y_4}{252.746} \]
Table A.6: Determination of Total Trihalomethanes

<table>
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<tr>
<th>Experiment Number</th>
<th>y1</th>
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<th>y3</th>
<th>y4</th>
<th>Y1</th>
<th>Y</th>
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<td>30.80</td>
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<td>0.667</td>
</tr>
<tr>
<td>3</td>
<td>42.20</td>
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<td>49.75</td>
<td>71.10</td>
<td>67.50</td>
<td>16.70</td>
<td>205.05</td>
<td>1.241</td>
</tr>
<tr>
<td>28</td>
<td>43.60</td>
<td>67.80</td>
<td>58.20</td>
<td>14.35</td>
<td>183.95</td>
<td>1.115</td>
</tr>
</tbody>
</table>

Note:

y1  [CHCl₃], ppb
y2  [CHCl₂Br], ppb
y3  [CHBr₂Cl], ppb
y4  [CHBr₃], ppb
Y1  [TTHM], ppb
Y   [TTHM], µmol/L

Experiment #20, missing data
Concentrations were measured 96 hours after chlorination
A.3 Filtration Pilot Plant

Procedure:
1. The Water sample was pumped to a coagulation tank (55 gals).
2. Coagulation agent (using approximately 200 ml Alum solution, 10%) was added.
3. The Tank stirring system was started-up at 100 rpm during 30 seconds.
4. The pH was adjusted to approximately 7.2 with NaOH (using approximately 14 ml NaOH, 50%).
5. Continuous stirring for 30 sec. at 100 rpm was allowed.
6. Then, stirring was slowed down to 5 rpm during 30 minutes.
7. The water was allowed to stand for sedimentation for about 45 min.
8. Water was decanted through the sand filter column at 2-4 gals/min/ft².
9. Filter effluent was collected and ready for the chlorination process.
Sand Filtration Column:

The sand filter column was arranged in ascendent particle size order through the column. Particle size had a specific diameter of 0.35-0.45 mm and uniformity coefficient of 1.75.
Appendix B

Statistical Analysis of Results
Table of Analysis of Variance for the Models Development.

Table B.1: Analysis of Variance (ANOVA) for TTHM Model #3

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Degrees of Freedom (df)</th>
<th>Sum of Squares (SS)</th>
<th>Mean Square (MS)</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Due to Regression</td>
<td>k-1</td>
<td>∑&lt;sub&gt;i=1&lt;/sub&gt; (Ŷ&lt;sub&gt;i&lt;/sub&gt; - Y)²</td>
<td>MS&lt;sub&gt;Reg&lt;/sub&gt;</td>
<td>MS&lt;sub&gt;Reg&lt;/sub&gt;/s²</td>
</tr>
<tr>
<td>About regression (residual)</td>
<td>n-k</td>
<td>∑&lt;sub&gt;i=1&lt;/sub&gt; (Y&lt;sub&gt;i&lt;/sub&gt; - Ŷ&lt;sub&gt;i&lt;/sub&gt;)²</td>
<td>s² = SS/(n-k)</td>
<td></td>
</tr>
<tr>
<td>Total, corrected</td>
<td>n-1</td>
<td>∑&lt;sub&gt;i=1&lt;/sub&gt; (Y&lt;sub&gt;i&lt;/sub&gt; - Y)²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.2: ANOVA for Residual Chlorine

<table>
<thead>
<tr>
<th>Source of Variation</th>
<th>Degrees of Freedom (df)</th>
<th>Sum of Squares (SS)</th>
<th>Mean Square (MS)</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Due to regression</td>
<td>k-1</td>
<td>∑&lt;sub&gt;i=1&lt;/sub&gt; (Ŷ&lt;sub&gt;2i&lt;/sub&gt;-Ŷ&lt;sub&gt;2&lt;/sub&gt;)²</td>
<td>MS&lt;sub&gt;Reg&lt;/sub&gt;</td>
<td>MS&lt;sub&gt;Reg&lt;/sub&gt;/s²</td>
</tr>
<tr>
<td>About regression (residual)</td>
<td>n-k</td>
<td>∑&lt;sub&gt;i=1&lt;/sub&gt; (Y&lt;sub&gt;2i&lt;/sub&gt;-Ŷ&lt;sub&gt;2i&lt;/sub&gt;)²</td>
<td>s² = SS/(n-k)</td>
<td></td>
</tr>
<tr>
<td>Total, corrected</td>
<td>n-1</td>
<td>∑&lt;sub&gt;i=1&lt;/sub&gt; (Y&lt;sub&gt;2i&lt;/sub&gt;-Ŷ&lt;sub&gt;2&lt;/sub&gt;)²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Correction factor</td>
<td>1</td>
<td>SS(b₀) = n(Ŷ&lt;sub&gt;2&lt;/sub&gt;)²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>n</td>
<td>∑&lt;sub&gt;i=1&lt;/sub&gt; (Y&lt;sub&gt;2i&lt;/sub&gt;)²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n = set of observations, k = set of parameters
<table>
<thead>
<tr>
<th>Observation Number</th>
<th>Observed Y, μmol/L</th>
<th>Predicted Y, μmol/L</th>
<th>Residual ((\hat{Y} - Y)), μmol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.503</td>
<td>0.46549</td>
<td>0.03751</td>
</tr>
<tr>
<td>2</td>
<td>0.677</td>
<td>0.72600</td>
<td>-0.04900</td>
</tr>
<tr>
<td>3</td>
<td>0.906</td>
<td>0.98154</td>
<td>-0.07554</td>
</tr>
<tr>
<td>4</td>
<td>1.301</td>
<td>1.25410</td>
<td>0.04690</td>
</tr>
<tr>
<td>5</td>
<td>0.601</td>
<td>0.62211</td>
<td>-0.02111</td>
</tr>
<tr>
<td>6</td>
<td>0.753</td>
<td>0.83575</td>
<td>-0.08275</td>
</tr>
<tr>
<td>7</td>
<td>1.718</td>
<td>1.60680</td>
<td>0.11120</td>
</tr>
<tr>
<td>8</td>
<td>1.667</td>
<td>1.83260</td>
<td>-0.16560</td>
</tr>
<tr>
<td>9</td>
<td>0.523</td>
<td>0.48823</td>
<td>0.03477</td>
</tr>
<tr>
<td>10</td>
<td>0.780</td>
<td>0.81229</td>
<td>-0.03229</td>
</tr>
<tr>
<td>11</td>
<td>0.905</td>
<td>1.00430</td>
<td>-0.09930</td>
</tr>
<tr>
<td>12</td>
<td>1.482</td>
<td>1.34040</td>
<td>0.14160</td>
</tr>
<tr>
<td>13</td>
<td>0.552</td>
<td>0.64484</td>
<td>-0.09284</td>
</tr>
<tr>
<td>14</td>
<td>0.876</td>
<td>0.92204</td>
<td>-0.04604</td>
</tr>
<tr>
<td>15</td>
<td>1.382</td>
<td>1.62960</td>
<td>-0.24760</td>
</tr>
<tr>
<td>16</td>
<td>2.027</td>
<td>1.91880</td>
<td>0.10820</td>
</tr>
<tr>
<td>17</td>
<td>0.509</td>
<td>0.46549</td>
<td>0.04351</td>
</tr>
<tr>
<td>18</td>
<td>0.715</td>
<td>0.81229</td>
<td>-0.09729</td>
</tr>
<tr>
<td>19</td>
<td>0.886</td>
<td>1.00430</td>
<td>-0.11830</td>
</tr>
<tr>
<td>20</td>
<td>0.718</td>
<td>0.64484</td>
<td>0.07316</td>
</tr>
<tr>
<td>21</td>
<td>0.974</td>
<td>0.83575</td>
<td>0.13825</td>
</tr>
<tr>
<td>22</td>
<td>1.796</td>
<td>1.60680</td>
<td>0.18920</td>
</tr>
<tr>
<td>23</td>
<td>1.899</td>
<td>1.91880</td>
<td>-0.01980</td>
</tr>
<tr>
<td>24</td>
<td>0.920</td>
<td>0.84883</td>
<td>0.07117</td>
</tr>
<tr>
<td>25</td>
<td>0.943</td>
<td>0.84883</td>
<td>0.09417</td>
</tr>
<tr>
<td>26</td>
<td>1.241</td>
<td>1.14900</td>
<td>0.09200</td>
</tr>
<tr>
<td>27</td>
<td>1.115</td>
<td>1.14900</td>
<td>-0.03400</td>
</tr>
</tbody>
</table>

\[
\text{SS} = 35.24168 \\
\text{Mean} = 1.050703
\]

\[
\text{SS}(b_0) = n(\bar{Y})^2 = 29.80741
\]

Total, corrected for mean \(\bar{Y} = 35.24168 - 29.80741 = 5.434269\)

\[
\text{SS, due to regression} = 5.434269 - 0.284271 = 5.14998
\]
### Table B.4: Observed, Predicted and Residual Values for Residual Chlorine.

<table>
<thead>
<tr>
<th>Observation Number</th>
<th>Observed Y2, ppm</th>
<th>Predicted Y2, ppm</th>
<th>(Ŷ2 - Y2), ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.87</td>
<td>0.68381</td>
<td>0.18619</td>
</tr>
<tr>
<td>2</td>
<td>1.28</td>
<td>1.74180</td>
<td>-0.46180</td>
</tr>
<tr>
<td>3</td>
<td>0.21</td>
<td>0.30100</td>
<td>-0.09100</td>
</tr>
<tr>
<td>4</td>
<td>0.87</td>
<td>1.19318</td>
<td>-0.32318</td>
</tr>
<tr>
<td>5</td>
<td>6.20</td>
<td>7.06892</td>
<td>-0.86892</td>
</tr>
<tr>
<td>6</td>
<td>12.60</td>
<td>11.00230</td>
<td>1.59770</td>
</tr>
<tr>
<td>7</td>
<td>7.00</td>
<td>5.92048</td>
<td>1.07952</td>
</tr>
<tr>
<td>8</td>
<td>10.20</td>
<td>9.35641</td>
<td>0.84359</td>
</tr>
<tr>
<td>9</td>
<td>0.83</td>
<td>0.43668</td>
<td>0.39332</td>
</tr>
<tr>
<td>10</td>
<td>1.20</td>
<td>0.80395</td>
<td>0.39605</td>
</tr>
<tr>
<td>11</td>
<td>0.40</td>
<td>0.05387</td>
<td>0.34613</td>
</tr>
<tr>
<td>12</td>
<td>0.70</td>
<td>0.25533</td>
<td>0.44467</td>
</tr>
<tr>
<td>13</td>
<td>7.58</td>
<td>6.82179</td>
<td>0.75821</td>
</tr>
<tr>
<td>14</td>
<td>10.80</td>
<td>10.06440</td>
<td>0.73560</td>
</tr>
<tr>
<td>15</td>
<td>7.10</td>
<td>5.67336</td>
<td>1.42664</td>
</tr>
<tr>
<td>16</td>
<td>8.10</td>
<td>8.41856</td>
<td>-0.31856</td>
</tr>
<tr>
<td>17</td>
<td>0.75</td>
<td>0.68381</td>
<td>0.06619</td>
</tr>
<tr>
<td>18</td>
<td>1.63</td>
<td>0.80395</td>
<td>0.82605</td>
</tr>
<tr>
<td>19</td>
<td>0.12</td>
<td>0.05387</td>
<td>0.06613</td>
</tr>
<tr>
<td>20</td>
<td>5.45</td>
<td>6.82179</td>
<td>-1.37179</td>
</tr>
<tr>
<td>21</td>
<td>9.80</td>
<td>11.00230</td>
<td>-1.20230</td>
</tr>
<tr>
<td>22</td>
<td>5.30</td>
<td>5.92048</td>
<td>-0.62048</td>
</tr>
<tr>
<td>23</td>
<td>7.00</td>
<td>8.41856</td>
<td>-1.41856</td>
</tr>
<tr>
<td>24</td>
<td>0.92</td>
<td>1.84735</td>
<td>-0.92735</td>
</tr>
<tr>
<td>25</td>
<td>0.79</td>
<td>1.84735</td>
<td>-1.05735</td>
</tr>
<tr>
<td>26</td>
<td>2.55</td>
<td>3.02022</td>
<td>-0.47022</td>
</tr>
<tr>
<td>27</td>
<td>2.80</td>
<td>3.02022</td>
<td>-0.22022</td>
</tr>
</tbody>
</table>

SS: 868.2109  Mean: 4.187037

SS Regression = 868.2109 - 18.09051 = 850.1204

A plot of Normal Probability for TTHM and Residual Chlorine can be found in the Figure B.1 and Figure B.2 (using data from Table B.3 and Table B.4).
Figure B.1: Normal Probability Plot for Residual Chlorine
Table B.5: Sum of Squares for Replicates (TTHM Formation and Residual Chlorine Models)

<table>
<thead>
<tr>
<th>Experiments # Replicated</th>
<th>Sum of Squares *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TTHM formation</td>
</tr>
<tr>
<td>1 + 17</td>
<td>0.0000</td>
</tr>
<tr>
<td>10 + 18</td>
<td>0.0021</td>
</tr>
<tr>
<td>11 + 19</td>
<td>0.0002</td>
</tr>
<tr>
<td>24 + 25</td>
<td>0.0003</td>
</tr>
<tr>
<td>26 + 27</td>
<td>0.0079</td>
</tr>
<tr>
<td>16 + 23</td>
<td>0.0080</td>
</tr>
<tr>
<td>13 + 20</td>
<td>0.0138</td>
</tr>
<tr>
<td>6 + 21</td>
<td>0.0244</td>
</tr>
<tr>
<td>7 + 22</td>
<td>0.0030</td>
</tr>
<tr>
<td>Total SS, Pure Error</td>
<td>0.05995</td>
</tr>
</tbody>
</table>

* Computed as follow for replicate 13 + 20, 1 degree of freedom

SS for replicate:

for TTHM formation \(= 0.5 \times (0.552 - 0.718)^2 = 0.0138\)

for Residual Chlorine \(= 0.5 \times (7.58 - 5.45)^2 = 2.2684\)
Appendix C

Regression Program
C PROGRAM REGRESS
  DIMENSION PAR(10), Y(56)
  COMMON X1(56),X2(56),X3(56),X4(56)
  WRITE(*,2)
  2 FORMAT(' GIVE THE NUMBER OF OBSERVATIONS = ?')
  READ(*,*)NOB
  WRITE(*,4)
  4 FORMAT(' GIVE THE NUMBER OF PARAMETERS = ?')
  READ(*,*)NPAR
  WRITE(*,3)
  3 FORMAT(' GIVE THE RESULTS FILE NAME ')
  WRITE(6,7)NPAR,NOB
  7 FORMAT(10X,' NPAR = ',12,20X,' NOB = ',12)
  WRITE(6,1)
  1 FORMAT(18X,' ** PARAMETERS VALUES **')
  DO 15 N=1,NPAR
  WRITE(*,11) N
  11 FORMAT(' GIVE THE PARAMETER VALUE (',12,',') = ?')
  READ(*,*) PAR(N)
  WRITE(6,8)N,PAR(N)
  8 FORMAT(20X,' PAR(',12,') = ',E9.3)
  15 CONTINUE
  WRITE(*,16)
  16 FORMAT(' GIVE THE DATA FILE NAME')
  READ(5,10)(Y(I),X1(I),X2(I),X3(I),X4(I),I=1,NOB)
  10 FORMAT(5(F9.3))
  WRITE(6,17)
  17 FORMAT(' Y = DEPENDENT VARIABLE',10X,'X = INDEPENDENT VARIABLES')
  WRITE(6,12)
  12 FORMAT(10X,'Y ',9X,'X1',10X,'X2',10X,'X3',10X,'X4')
  WRITE(6,13)(Y(I),X1(I),X2(I),X3(I),X4(I),I=1,NOB,1)
  13 FORMAT(5(3X,F9.3))
  CALL LS(NOB,Y,NPAR,PAR,0)
  STOP
END

NUMBER OF WARNINGS IN PROGRAM UNIT: 0
NUMBER OF ERRORS IN PROGRAM UNIT: 0

C SUBROUTINE MODEL(PAR,F,NOB,NPAR)
  DIMENSION PAR(NPAR),F(NOBS)
  COMMON X1(56),X2(56),X3(56),X4(56)
  DO 1 I=1,NOB
  1 F(I)=PAR(1)/X4(I)+PAR(2)*X3(I)+PAR(3)*(X2(I)*X3(I))+PAR(4)*X4(I)+PAR(5)*X3(I)+PAR(6)*X1(I)
  CONTINUE
RETURN
END
53 C
54 SUBROUTINE DIF(PAR,Z,FO,NOB,NPAR,DEL)
55 DIMENSION PAR(NPAR),Z(NOB,NPAR),FO(NOB),DEL(NPAR)
56 RETURN
57 END

72

* IDIF
69 COMMON/BLOK2/IDER
70 LOGICAL LG, L1
71 DATA III(0)/
72 MOB=200
73 MPAR=30
74 FINF=1.0030
75 IF(IRED.GE.1)GO TO 100
76 DO 101 I=1,NPAR
77 LG=PAR(I).EQ.0
78 IF(LG)WRITE(6,25)I
79 IF(LG)STOP
80 25 FORMAT('REPARAMETER PAR(',12,') IS EQUAL TO ZERO')
81 DEL(I)=-0.01
82 CHMAX(I)=0.2*ABS(PAR(I))
83 BNWLW(I)=-FINF
84 101 BNUP(I)=FINF
85 REDA=1.0E-4
86 RSSTOL=1.0E-3
87 WRITE(*,98)
88 98 FORMAT('GIVE THE MAXIMUM ITERATION NUMBER')
89 READ(*,*)ITMAX
90 WRITE(6,99)ITMAX
91 99 FORMAT('// MAXIMUM ITERATION ARE = ','12)
92 LISTS=3
93 IDIF=1
94 IF(IRED.LE.-1)RETURN
95 100 CONTINUE
96 III=III+1
ZERO=0
WRITE(6,14)II,NOB,NPAR
14  FORMAT(*START OF PROBLEM NO.12, WITH OBSERVATIONS AND ' PARAMETERS'\' Version 4 of LS, AUGUST 1971\*','12,15,' (',15, ' WAS USED'))
M=MOB
IF(MOB.GT.MOB)WRITE(6,15)NOB,M
15  FORMAT('INCREASE THE VALUE OF MOB TO',15,' (',15, ' WAS USED'))
M=NPAR
IF(NPAR.GT.NPAR)WRITE(6,16)NPAR,M
16  FORMAT('INCREASE THE VALUE OF NPAR TO',15,' (',15, ' WAS USED'))
IF((NOB.GT.MOB).OR.(NPAR.GT.NPAR))STOP
WRITE(6,7)(BDUP(I),I=1,NPAR)
7  FORMAT(' BDUP(I) = ',5E12.5)
WRITE(6,8)(PAR(I),I=1,NPAR)
8  FORMAT(' PAR(I) = ',5E12.5)
WRITE(6,6)(BNDLW(I),I=1,NPAR)
6  FORMAT(' BNDLW(I) = ',5E12.5)
WRITE(6,651)
11  WRITE(6,11)(DEL(I),I=1,NPAR)
11  FORMAT(' DEL(I) = ',5E12.5)
WRITE(6,13)(CHMAX(I),I=1,NPAR)
13  FORMAT(' CHMAX(I) = ',5E12.5)
WRITE(6,17)REDA,RSTSTL,ITMAX,LISTS,IDIF
17  FORMAT('REDA = ',E12.4,' RSTSTL = ',E12.4,' ITMAX = ',I4,
* ' LISTS = ',I3,' IDIF = ',I3)
FMIN=1.
DO 4 I=1,NPAR
4   FMIN=MIN(FMIN,ABS(DEL(I)))
LG=PAR(I).LT.BNDLW(I).OR.PAR(I).GT.BNDUP(I)
IF(LG)WRITE(6,18)I
18   FORMAT(' PARAMETER PAR(',I2,'.) IS OUTSIDE OF BOUNDS')
IF(FMIN.LT.1.0E-35)WRITE(6,27)
27   FORMAT('FMIN IS OUTSIDE OF BOUNDS')
IF(FMIN.GE.1.0E-35)WRITE(6,26)
26   FORMAT('FMIN IS NOT OUTSIDE OF BOUNDS')
ITNO=1
NPAR=NPAR+1
IF(NPAR.GT.0)WRITE(6,3)ITNO,NFUNC
3   WRITE(6,3)ITNO,NFUNC
IF(NPAR.GT.0)WRITE(6,4)NPAR
4   WRITE(6,4)NPAR
FORMAT('OSTART ITERATION NO.13, NO. OF FUNCTION CALLS',I4)
IDER=0
CALL MODEL(PAR,FO,NOB,NPAR)
IF(NFUNC.GT.0)WRITE(6,1)NPAR
WRITE(6,2)(PAR(I),I=1,NPAR)
2   FORMAT(' PAR(I) = ',5E12.6)
ITNO=ITNO+1
IF(FMIN.LT.1.0E-35)CALL DIF(PAR,Z,FO,NOB,NPAR,NPAR,DEL)
5   FORMAT('DIF(PAR,Z,FO,NOB,NPAR,NPAR,DEL')
DO 5 IOB=1,NOB
5   Z(IOB,NPAR)=FO(IOB)+OBS(IOB)
DO 490 IPAR=1,NPAR
50   IF(CABS(DIF(IPAR)).LT.1./FINF)GO TO 490
490  IF(CHMAX(IPAR).GE.0.AND.BNDUP(IPAR)-BNDLW(IPAR).GE.1./FINF)
* GO TO 410
DO 490 IOB=1,NOB
500  Z(IOB,IPAR)=0.0
GO TO 490
LG=DEL(IPAR).GT.0
LG=.NOT.LG.AND.ABS(PAR(IPAR)*DEL(IPAR)).LE.1.E-20
157  IF(LG) WRITE(6,60) IPAR
158  60  FORMAT(' THE VALUE OF PAR(',13,' IS TOO SMALL FOR
159  *DETERMINING THE DERIVATIVE')
160  IF(LG) STOP
161  PARD=PAR(IPAR)
162  IF(LG) DELPAR=DELPAR(IPAR)
163  IF(.NOT.LG) DELPAR=ABS(PAR(IPAR)*DELPAR(IPAR))
164  JDIF=JDIF
165  $1+BNDUP(IPAR)+PARD+DPAR
166  S2=PARD+DPAR+BNDLW(IPAR)
167  IF(S2.LT.0.AND.S2.GT.S1.AND.IDIF.GT.0) JDIF=-1
168  IF(S2.LT.0.AND.S1.GT.IDIF.LT.0) JDIF=1
169  IF(JDIF.LT.0) GO TO 420
170  PAR(IPAR)=AMAX1(PARD+DPAR,BNDUP(IPAR))
171  WRITE(6,434) PAR(IPAR)
172  C FORMAT(' PAR(',1,'= ',13,4)
173  DENOM=PAR(IPAR)
174  CALL MODEL(PAR,FUP,N0B,NPAR)
175  NFUNC=NFUNC+1
176  GO TO 440
177  420  DENOM=PARD
178  DO 430 I0B=1,N0B
179  430  FUP(I0B)=FOC(I0B)
180  440  IF(JDIF.GT.0) GO TO 450
181  PAR(IPAR)=AMAX1(PARD+DPAR,BNDLW(IPAR))
182  C WRITE(6,435) PAR(IPAR)
183  DENOM=DENOM-PAR(IPAR)
184  CALL MODEL(PAR,FLW,N0B,NPAR)
185  NFUNC=NFUNC+1
186  GO TO 470
187  450  DENOM=DENOM-PARD
188  DO 460 I0B=1,N0B
189  FLW(I0B)=FOC(I0B)
190  C WRITE(6,492) FLW(I0B),FUP(I0B)
191  460  CONTINUE
192  470  PAR(IPAR)=PARD
193  DO 480 I0B=1,N0B
194  Z(I0B,IPAR)=(FUP(I0B)-FLW(I0B))/DENOM
195  C WRITE('*,485)Z(I0B,IPAR),IPAR
196  480  CONTINUE
197  490  CONTINUE
198  DO 200 IPAR=1,NPAR1
199  DO 200 JPAR=1,NPAR1
200  X=0.
201  DO 19 I0B=1,N0B
202  19  X=X+2*(I0B,IPAR)*Z(I0B,JPAR)
203  A(IPAR,JPAR)=X
204  20  A(JPAR,IPAR)=X
205  IF(ITNO.EQ.2) WRITE(6,12) A(NPAR1,NPAR1)
206  12  FORMAT(' A INITIAL SUM OF SQUARES= ',13,4)
207  21  IF(LISTS.LE.D) GO TO 501
208  WRITE(6,22)
209  22  FORMAT('*/ MATRIX OF NORMAL EQUATIONS */')
210  DO 49 I0B=1,NPAR1
211  49  WRITE(6,50)(A(I,J),J=1,NPAR1)
212  50  FORMAT(1X,15D12.4)
213  501 NES=0
214  NTRANS=0
215  SSB=A(NPAR1,NPAR1)
216  DO 502 I=1,NPAR1
217   LSTP(I)=0
218   LBIU(I)=0
219   PARB(I)=PAR(I)
220   SPOA(I)=REDA*A(I,1)
221   SSRED=0.
222   JBUI=0
223   NPIV=0
224   DO 510 I=1,NPAR
225   IF(LSTP(I).NE.0.OR.A(I,1).LE.SPOA(I).OR.ABS(CHMAX(I)))
226      ".LT.1./FINF) GO TO 510
227      TRED=A(I,NPAR)**2/A(I,1)
228      IF(TRED.LT.SSRED)GO TO 510
229      JB=0
230      FACTO=FINF
231      DO 508 J=1,NPAR
232      IF(J.NE.1)GO TO 504
233      REF=PAR(I)
234      DENOM=A(I,NPAR)/A(I,1)
235      GO TO 505
236   504   IF(LSTP(J).EQ.0) GO TO 508
237      REF=PAR(J)+A(J,NPAR)
238      DENOM=A(J,1)*A(I,NPAR)/A(I,1)
239   505   IF(DENOM.GT.1./FINF)GO TO 506
240      IF(DENOM.GT.-1./FINF)GO TO 508
241      IF(BNDLW(J).LE.-FINF)GO TO 508
242      TFACT=(BNDLW(J)-REF)/DENOM
243      IJ=J
244      GO TO 507
245   506   IF(BNDUP(J).GE.FINF)GO TO 508
246      TFACT=(BNDUP(J)-REF)/DENOM
247      IJ=J
248   507   IF(FACTO.LE.TFACT)GO TO 508
249      FACTO=TFACT
250      JB=1J
251   508   CONTINUE
252      IF(FACTO.GT.1)GO TO 509
253      TRED=TRED+FACTO*(2.-FACTO)
254   509   IF(TRED.LT.SSRED)GO TO 510
255      SSRED=TRED
256      FMLAX=FACTO
257      JBUI=JB
258      NPIV=1
259   510   CONTINUE
260      IF(NPIV.EQ.0.OR.FLAX.LT.1./FINF)GO TO 530
261      NTRANS=NTRANS+1
262      IF(FLMAX.LE.1./GO TO 52
263      NES= NES+1
264      LSTP(NPIV)=NPIV
265      LBUI(NPIV)=0
266      GO TO 57
267   52   IRESP=ABS(JBUI)
268      IF(IRESP.NE.NPIV)NES=NES+1
269      LSTP(IRESP)=0
270      DPIV=FACTO*A(NPIV,NPAR1)/A(NPIV,NPIV)
271      PAR(NPIV)=PAR(NPIV)+DPIV
272      PAR(IRESP)=BNDLW(IRESP)
273      IF(JBUI.GT.0)PAR(IRESP)=BNDUP(IRESP)
274   57   DO 58 I=1,NPAR
275      IF(PAR(I)-BNDLW(I).LE.1./FINF.AND.LSTP(I).EQ.0)LBUI(I)=I
276   58   IF(BNDUP(I)-PAR(I).LE.1./FINF.AND.LSTP(I).EQ.0)LBUI(I)=I
277 IF(LSTSP.EQ.0) WRITE(6,59)(LBIU(I),I=1,NPAR)
278 FORMAT(1X('
LBIU =',2,15))
279 IF(LSTSP.EQ.0)(LSTP(I),I=1,NPAR)
280 61 FORMAT(' LSTPS =',2,15)
281 IF(LSTSP.EQ.0)(LSTP(I),I=1,NPAR)
282 IF(FLMAX.LE.1) GO TO 70
283 62 IF(FLMAX.LE.1) NPIV=IRESP
284 PIVOT=A(NPIV,NPIV)
285 ANPIV,NPIV=1.000
286 DO 512 J=1,NPAR
287 512 A(NPIV,J)=A(NPIV,J)/PIVOT
288 DO 513 I=1,NPAR
289 IF(I.EQ.NPIV) GO TO 520
290 CMULT=A(I,NPIV)
291 DO 519 J=1,NPAR
292 519 IF(J.NE.NPIV) A(I,J)=A(I,J)-CMULT*A(NPIV,J)
293 A(I,NPIV)=A(I,NPIV)/PIVOT
294 520 CONTINUE
295 521 IF(LSTSP.LT.5) GO TO 503
296 WRITE(6,30)
297 30 FORMAT('TRANSFORMED MATRIX INCLUDING INVERSE OF
298 *EQUATIONS THAT ARE NOW SOLVED')
299 DO 522 I=1,NPAR
300 522 WRITE(6,50) A(I,J),J=1,NPAR
301 GO TO 503
302 DO 70 A(NPAR1,NPAR)=A(NPAR1,NPAR)-SSRED
303 DO 76 J=1,NPAR
304 A(I,NPAR1)=A(I,NPAR1)-DPIV*ANPIV
305 LG1=LSTP(I),NE.0
306 LG=PAR(I),GT.BNDUP(I)
307 IF(LG .AND. LG1) A(I,NPAR1)=0.0
308 LG=PAR(I),LT.BNDLW(I)
309 IF(LG .AND. LG1) A(I,NPAR1)=0.0
310 LG=PAR(I),GT.BNDLW(I)
311 IF(LG .AND. LG1) A(I,NPAR1)=0.0
312 LG1=A(NPAR1,1)=A(I,NPAR1)
313 76 IF (.NOT. LG1) A(NPAR1,1)=A(I,NPAR1)
314 73 IF(NPIV.EQ.IRESP) GO TO 521
315 A(NPAR1,1)=0.00
316 GO TO 62
317 IF(NTRANS.GT.0) GO TO 531
318 561 WRITE(6,542)
319 562 FORMAT('ONWARDS PARAMETER CHANGES PERMITTED. INSPECT BOUNDS AND CHMAX
320 **ARRAY')
321 STOP
322 531 SSE1=A(NPAR1,NPAR)
323 550 DO 552 I=1,NPAR
324 IF(LSTP(I),EQ.0) A(I,NPAR1)=0
325 A(I,NPAR1)=A(I,NPAR1)+PAR(I)-PARB(I)
326 552 CONTINUE
327 ILAM=0
328 IFAM=1
329 ILMAX=0
330 FLMAX=FINF
331 QMAX=FINF
332 DO 536 I=1,NPAR
333 ABSA=ABS(A(I,NPAR1))
334 IF(ABSAT.I.LT.1./FINF) GO TO 536
335 QLAM=ABS(ACHMAX(I))
336 IF(QCHMAX(I).LE.ZERO) QLAM=QLAM*DABS(PAR(I))
337 IF(FLAM*ABSA.LE.GLAM)GO TO 534
338 ILM=1
339 FLAM=GLAM/ABSA
340 534 IF(AA(1,NPAR).LT.ZERO)QMAX=BNDUP(I)*PAR(I)
341 IF(AA(1,NPAR).LT.ZERO)QMAX=PAR(I)*BNDL(I)
342 IF(QMAX.GE.FLMAX*ABSA)GO TO 536
343 ILMAX=1
344 FLMAX = QMAX/ABSA
345 536 CONTINUE
346 IF(FLAM.EQ.0.0)GO TO 547
347 WRITE(6,538)ILAM,FLAM
348 538 FORMAT(12OPARAMETER',I4,1,'LIMITS THE CORRECTIONS TO',E12.4,
349 ' TIMES THE GAUSS-NEWTON VALUES')
350 547 IF(FLMAX.LT.1.AND.ILMAX.LE.IIAM)WRITE(6,538)ILMAX,FLMAX
351 548 IF(FLAM.LT.1.FINF)GO TO 541
352 560 SBEST=SSB
353 FBEST=0.0
354 FLR=2.*FINF
355 SSP=SS1
356 SS(1)=SSB
357 FL(1)=0.0
358 SS(2)=1.01*FINF
359 FL(2)=1.01*FLMAX
360 SS(3)=1.02*FINF
361 FL(3)=1.02*FLMAX
362 FLT=FLAM
363 KEY=0
364 LG=.TRUE.
365 561 DO 590 IGRID=1,ILMAX
366 558 DO 562 I=1,NPAR
367 PAR(I)=PAR(I)+FLT*A(1,NPAR)
368 IF(PAR(I).GT.BNDUP(I))PAR(I)=BNDUP(I)
369 562 IF(PAR(I).LT.BNDL(I))PAR(I)=BNDL(I)
370 IDEIR=-1
371 CALL MODEL(PAR,F,NOB,NPAR)
372 NFUNC=NFUNC+1
373 SST=0.
374 DO 563 IOB=1,NOB
375 DF=ABS(F(IOB)-OBS(IOB))
376 IF(DF.GT.1.E15)WRITE(6,566)IOB,F(IOB)
377 566 FORMAT(1F('I',I3,'=\',E10.3,'IS TOO LARGE'))
378 IF(DF.GT.1.E15)STOP
379 563 SST=SST+DF**2
380 SSU=SST
381 LG=LG.AND.SST.GT.SSB
382 IF(KEQ.EQ.1)GO TO 581
383 IF(LSTG.EQ.4)WRITE(6,564)FLT,SST,IGRID,FLR,SSP
384 564 FORMAT('OFLT=',E13.5,' SST=',E13.5,' IGRID=',I3,' FLR=',D11.5,
385 ' SSP=',E13.5)
386 IF((ABS(FLT-1.).GT.RSS0L.AND.ABS(FLT-FLMAX).GT.RSS0L).OR.
387 *ABS(ABS-SS1).GT.ABS(ABS1)*RSS0L.OR.LG)GO TO 565
388 FLR=FLT
389 GO TO 581
390 565 INS=0
391 K=0
392 DO 575 I=1,3
393 IF(FL(I).GT.FLT.AND.INS.EQ.0)INS=I
394 IF(INS.GT.0)K=1
395 IK=IK+K
396 FD(IK)=FL(I)
397 575 SD(IK)=SS(I)
398 IF(INS.EQ.0)INS=4
399 FD(INS)=FLT
400 SD(INS)=SST
401 K=0
402 IF(SD(2).GT.SD(3).OR.INS.EQ.4).AND.1GRID.GT.2)K=1
403 IF(SD(1).LE.SD(2))K=0
404 DO 576 I=1,3
405 618 K=I*K
406 FL(I)=FD(IK)
407 576 SS(I)=SD(IK)
408 IF(LISTS.GE.6)WRITE(6,SD77)FD(J),J=1,4
409 IF(LISTS.GE.6)WRITE(6,SD68)SD(J),J=1,4
410 577 FORMAT(' FD TABLE ','E13.5')
411 568 FORMAT(' SD TABLE ','E13.5')
412 IF(SST.GE.SBEST)GO TO 578
413 SBEST=SST
414 FBEST=FLT
415 578 IF(FL(3).LE.FLMAX)GO TO 583
416 IF(SST(1).LE.SS(2))GO TO 587
417 FLT=0.1*FL(1)+0.9*FL(2)
418 GO TO 590
419 583 DENOM=(FL(3)-FL(1))*((SS(2)-SS(1))+1*(FL(1)-FL(2))*SS(3)
420 "-SS(1))
421 IF(DENOM.LE.1./FINF.AND.FL(3).LT.FINF)GO TO 584
422 SSP=FINF
423 IF(SS(1).GT.SS(2))GO TO 585
424 587 FLT=0.9*FL(1)+0.1*FL(2)
425 GO TO 590
426 585 FLT=FLMAX
427 IF(FL(3).GE.0.98*FLMAX)FLT=0.1*FL(2)+0.9*FL(3)
428 IF(FL(3).LT.0.49*FLMAX)FLT=2.*FL(3)
429 GO TO 590
430 584 FOLD=FLT
431 FLR=((FL(3)**2-FL(1)**2)*((SS(2)-SS(1))+1*(FL(1)**2-FL(2)**2)*
432 "SS(3)-SS(1))/2./DENOM
433 IF(FLR.GE.FLMAX)FLR=FLMAX
434 IF(FLR.LE.FL(1))FLR=FL(1)
435 SSR=SS(1)+(SS(2)-SS(1))*(FLR-FL(1))*(FLR-FL(3))/(FL(2)
436 "+FL(1)/FL(2)-FL(3))+(SS(3)-SS(1))*(FLR-FL(1))*
437 *(FLR-FL(2))/(FL(3)-FL(1))/(FL(3)-FL(2))
439 DABS(KSTOL*FLR))GO TO 580
440 IF(SSR.LT.0.OR.FLR.LE.FL(1).OR.FLR.GT.FL(3).OR.LG)GO TO 580
441 FL=FLR
442 KEY=1
443 GO TO 558
444 581 WRITE(6,SD79)GRID,FLR,SSR
445 579 FORMAT(' SEARCH CONVERGED AFTER ',15,' CYCLES, WITH LAMBDA ='
446 " ',E13.5,' AND SSA=',E13.5)
447 GO TO 626
448 580 SSP=SSR
449 582 FLT=0.9*FL(1)+0.1*FL(2)
450 IF(FLR.GT.FLT)FLT=FLR
451 FT=0.1*FL(1)+0.9*FL(2)
452 IF(FLR.GT.FT)FLT=FT
453 FT=0.9*FL(2)+0.1*FL(3)
454 IF(FLR.GT.FT)FLT=FT
455 IF(FLR.GE.FT)FLT=FLR
456 FT=0.1*FL(2)+0.9*FL(3)
IF(FLR.GT.FL)FL=FT
IF(FLR.GT.FL(3))GO TO 585
590 CONTINUE

IGRID=ITMAX+1
WRITE(6,591)ITMAX,FBEST,SBEST
591 FORMAT(/'SEARCH TOOK THE FULL',I4,' CYCLES BEST TRIAL POINT LAM')
593 'BDA=',E13.5,' SQ=',E13.5)
594 FLR=FBEST
595 SSR=SBEST
596 DO 626 I=1,NPAR
PAR(I)=PARB(I)+A(I,NPAR1)*FLR
626 CONTINUE

IF(SSB.LT.SSR)WRITE(6,629)SSR,SSB
629 FORMAT(15,E15.8,' OF PREVIOUS ITERATION')
630 IF(DGML.EQ.0.D0)I=1,NPAR
633 IF(LSTP(I).NE.0)A(I,NPAR1)=DSQRG(A(I,I))
634 DO 630 I=1,NPAR
635 WRITE(6,631)

631 FORMAT(15,E15.8,' OF LINEAR CONFIDENCE LIMITS')
633 *AS FOLLOWS')
635 PRINT 'J1=',NPAR+7/8
637 DO 650 J2=1,J1
638 I2=MINT(NPAR,J2+8)
639 PRINT 'I2=',I2
640 DO 650 I=1,I2
PAR(I)=PAR(I)+PARB(I)
650 CONTINUE

651 IF(LSTP(I).EQ.0)PARB(I)=FINF
652 WRITE(6,633)PARB(I),I=11,12
653 FORMAT(15,E15.8,2,40D12.5)
654 WRITE(6,649)PARB(I),I=11,12
655 DO 650 I=11,12
PARB(I)=2*PAR(I)-PARB(I)
656 WRITE(6,635)PARB(I),I=11,12
657 FORMAT(15,E15.8,2,40D12.5)
658 WRITE(6,656)SEXT,NOW,NDF
659 FORMAT(15,E15.8,2,40D12.5)
660 DO 650 I=1,NPAR
661 DO 650 J=1,11
662 IF(LSTP(I)*LSTP(J).EQ.0)A(I,J)=A(I,J)/A(I,NPAR1)/A(J,NPAR1)
663 DO 650 J=1,11
664 IF(LSTP(I)*LSTP(J).EQ.0)A(I,J)=1.E8
665 WRITE(6,641)
666 IF(LSTP(I)*LSTP(J).EQ.0)A(I,J)=1.E8
667 WRITE(6,641)
517  J1=(NPAR+9)/10
518  DO 660 J2=1,J1
519  652  FORMAT(1X)
520  11=(J2-1)*10+1
521  12=MIND(NPAR,J2*10)
522  DO 660 I=11,NPAR
523  11=MIND(I,12)
524  WRITE(6,652)
525  660  WRITE(6,655)(A(I,J),J=11,II)
526  655  FORMAT(1H ,5X,10(F7.4,3X))
527  651  FORMAT(1H0)
528  661  IF(LISTS.LT.3)GO TO 666
529  666  IDER=-2
530  CALL MODEL(PAR,F,NOB,NPAR)
531  NFUNC=NFUNC+1
532      X=0
533  680  DO 650 I=1,NOB
534  660  WRITE(6,662)
535  662  WRITE(6,663)(F(I),I=1,NOB)
536  663  FORMAT(1X,14E12.5)
537  670  WRITE(6,665)
538  675  FORMAT(1H0 FINAL FUNCTION VALUES'/10H0 )
539  670  WRITE(6,663)(F(I),I=1,NOB)
540  675  FORMAT(1H0 RESIDUALS'/10H0 )
541  670  WRITE(6,663)(F(I),I=1,NOB)
542  680  WRITE(6,665)
543  685  FORMAT(1H0 FINAL SUM OF SQUARES *=',D12.4)
544  WRITE(6,671)III,NFUNC
545  671  FORMAT(1H0 END OF PROBLEM NO.*,I4,,' NO. OF FUNCTION CALLS=*,I4)
546  680  RETURN
547  END

NUMBER OF WARNINGS IN PROGRAM UNIT: 0
NUMBER OF ERRORS IN PROGRAM UNIT: 0
NUMBER OF WARNINGS IN COMPILATION : 0
NUMBER OF ERRORS IN COMPILATION : 0
Appendix D

Regression Program Results for TTHM
** INITIAL PARAMETER **

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** DEPENDENT VARIABLE **

** INDEPENDENT VARIABLES **

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** MAXIMUM ITERATION ARE = 20 **

** MODEL: ** $\text{ITHM} = f(x_1, x_2, x_3, x_4) = Y$

$$Y = \text{PAR}(1) + \text{PAR}(2)/x_4 + \text{PAR}(3)\log(x_2) + \text{PAR}(4)\times x_3 + \text{PAR}(5)\times (x_2\times x_3) + \text{PAR}(6)\times x_1$$
START OF PROBLEM NO. 1 WITH 27 OBSERVATIONS AND 6 PARAMETERS

VERSION 4 OF LS, AUGUST 1971

**BDUP(1) =** .10000E+31 .10000E+31 .10000E+31 .10000E+31 .10000E+31 .10000E+31  
**PAR(1) =** .10000E+01 .10000E+01 .10000E+01 .10000E+01 .10000E+01 .10000E+01  
**BNDLW(1) =** -.10000E+31 -.10000E+31 -.10000E+31 -.10000E+31 -.10000E+31 -.10000E+31  
**DEL(1) =** -.10000E-01 -.10000E-01 -.10000E-01 -.10000E-01 -.10000E-01 -.10000E-01  
**CHMAX(1) =** .20000E+00 .20000E+00 .20000E+00 .20000E+00 .20000E+00 .20000E+00  
**REDA =** .10000E-03 **RSTOL =** .10000E-02 **ITMAX =** 20 **LISTS =** 3 **IDIF =** 1

SUBROUTINE DIF IS NOT USED

START ITERATION NO. 1 NO. OF FUNCTION CALLS 0  
**PAR(1) =** .100000E+01 .100000E+01 .100000E+01 .100000E+01 .100000E+01 .100000E+01  
**INITIAL SUM OF SQUARES =** .1895D+05

**MATRIX OF NORMAL EQUATIONS**

\[
\begin{array}{ccccccc}
0.27000 \times 10^2 & 0.72370 \times 10^2 & 0.53170 \times 10^2 & 0.53000 \times 10^2 & 0.38820 \times 10^3 & 0.11230 \times 10^3 & -0.67760 \times 10^3 \\
0.72370 \times 10^2 & 0.23320 \times 10^3 & 0.14150 \times 10^3 & 0.14460 \times 10^3 & 0.10430 \times 10^4 & 0.31850 \times 10^3 & -0.18750 \times 10^4 \\
0.53170 \times 10^2 & 0.14150 \times 10^3 & 0.10570 \times 10^3 & 0.10450 \times 10^3 & 0.78040 \times 10^3 & 0.22050 \times 10^3 & -0.13480 \times 10^4 \\
0.53000 \times 10^2 & 0.14460 \times 10^3 & 0.10450 \times 10^3 & 0.12800 \times 10^3 & 0.93950 \times 10^3 & 0.22110 \times 10^3 & -0.15300 \times 10^4 \\
-0.38820 \times 10^3 & 0.10430 \times 10^4 & 0.78040 \times 10^3 & 0.93950 \times 10^3 & 0.71660 \times 10^4 & 0.16120 \times 10^4 & -0.11460 \times 10^5 \\
-0.11230 \times 10^3 & 0.31850 \times 10^3 & 0.22050 \times 10^3 & 0.22110 \times 10^3 & 0.16120 \times 10^4 & 0.48160 \times 10^3 & -0.28450 \times 10^4 \\
-0.67760 \times 10^3 & -0.18750 \times 10^4 & -0.13480 \times 10^4 & -0.15300 \times 10^4 & -0.11460 \times 10^5 & -0.28450 \times 10^4 & 0.18950 \times 10^5 \\
\end{array}
\]

PARAMETER 1 LIMITS THE CORRECTIONS TO .7273E-01 TIMES THE GAUSS-NEWTON VALUES

SEARCH CONVERGED AFTER 6 CYCLES, WITH LAMBDA = .10000E+01 AND SSQ = .28420E+00

START ITERATION NO. 2 NO. OF FUNCTION CALLS 14  
**PAR(1) =** -.174986E+01 -.347537E+01 .696177E+00 -.390331E+00 .781290E-01 .280353E+00

**MATRIX OF NORMAL EQUATIONS**

\[
\begin{array}{ccccccc}
0.27000 \times 10^2 & 0.72370 \times 10^2 & 0.53170 \times 10^2 & 0.53000 \times 10^2 & 0.38820 \times 10^3 & 0.11230 \times 10^3 & 0.19790 \times 10^2 \\
0.72370 \times 10^2 & 0.23320 \times 10^3 & 0.14150 \times 10^3 & 0.14460 \times 10^3 & 0.10430 \times 10^4 & 0.31850 \times 10^3 & 0.88460 \times 10^2 \\
0.53170 \times 10^2 & 0.14150 \times 10^3 & 0.10570 \times 10^3 & 0.10450 \times 10^3 & 0.78040 \times 10^3 & 0.22050 \times 10^3 & 0.22260 \times 10^2 \\
0.53000 \times 10^2 & 0.14460 \times 10^3 & 0.10450 \times 10^3 & 0.12800 \times 10^3 & 0.93950 \times 10^3 & 0.22110 \times 10^3 & 0.22010 \times 10^3 \\
-0.38820 \times 10^3 & 0.10430 \times 10^4 & 0.78040 \times 10^3 & 0.93950 \times 10^3 & 0.71660 \times 10^4 & 0.16120 \times 10^4 & 0.24780 \times 10^1 \\
-0.11230 \times 10^3 & 0.31850 \times 10^3 & 0.22050 \times 10^3 & 0.22110 \times 10^3 & 0.16120 \times 10^4 & 0.48160 \times 10^3 & 0.72330 \times 10^2 \\
-0.67760 \times 10^3 & -0.18750 \times 10^4 & -0.13480 \times 10^4 & -0.15300 \times 10^4 & -0.11460 \times 10^5 & -0.28450 \times 10^4 & 0.28420 \times 10^0 \\
\end{array}
\]

SEARCH CONVERGED AFTER 1 CYCLES, WITH LAMBDA = .10000E+01 AND SSQ = .28419E+00
BEST PARAMETER VALUES AND 2-SIGMA CONFIDENCE LIMITS ESTIMATED BY LINEARIZATION FOR THE INDIVIDUAL PARAMETERS ARE AS FOLLOWS:

UPR(I) = -.62868D+00 .20194D-01 .12238D+01 -.14980D+00 .11030D+00 .36825D+00
PAR(I) = -.17457D+01 -.34515D-01 .69479D+00 -.39037D+00 .78112D-01 .27995D+00
LWR(I) = -.28627D+01 -.89224D-01 .16578D+00 -.63094D+00 .45926D-01 .19165D+00

STANDARD ERROR OF WEIGHTED RESIDUALS = .11633E+00 ESTIMATED WITH 27 RESIDUALS AND 21 DEGREES OF FREEDOM.

NORMALIZED CORRELATION MATRIX

1.0000
.1683 1.0000
-.9642 -.0589 1.0000
-.8551 -.1180 .8741 1.0000
.8591 .1034 -.8956 -.9801 1.0000
-.3520 -.7231 .1241 .1175 -.1136 1.0000

FINAL FUNCTION VALUES

.46549E+00 .72600E+00 .98154E+00 .12541E+01
.62211E+00 .83575E+00 .16068E+01 .18326E+01
.48823E+00 .12229E+01 .10043E+01 .13404E+01
.64484E+00 .92206E+00 .16296E+01 .19188E+01
.46549E+00 .11229E+00 .10043E+01 .44841E+00
.83575E+00 .16068E+01 .19188E+01 .84883E+00
.84883E+00 .11490E+01 .11490E+01

RESIDUALS

-.37509E-01 .49003E-01 .75541E-01 -.46864E-01
-.21107E-01 .82751E-01 -.11117E+00 .16556E+00
-.34772E-01 .32291E-01 .99278E-01 -.14158E+00
.92844E-01 .46039E-01 .24757E+00 -.10815E+00
-.43509E-01 .97291E-01 .11828E+00 -.73156E-01
-.13825E+00 -.18917E+00 .19847E-01 .71166E-01
-.94166E-01 -.91969E-01 .34031E-01

FINAL SUM OF SQUARES = .2842D+00

END OF PROBLEM, NO. OF FUNCTION CALLS = 23