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Ms. W. F. Perrin, Technical Information Officer
U. S. Department of Energy
Savannah River Operations Office
Aiken, SC 29801

Dear Ms. Perrin:

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I. DETAILS OF REQUEST FOR RELEASE

WSRC-RP-89-786, "AN EMPIRICAL COMPUTER MODEL OF THE F-AREA A-LINE NITROGEN OXIDES ABSORPTION COLUMN (F 8 COLUMN) (U)," By K. L. Shanahan and S. F. Peterson.

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Analytical Development
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AN EMPIRICAL COMPUTER MODEL OF THE F-AREA A-LINE NITROGEN OXIDES ABSORPTION COLUMN (F-8 COLUMN) (U)

K. L. Shanahan and S. F. Peterson

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AN EMPIRICAL COMPUTER MODEL OF THE F-AREA A-LINE NITROGEN OXIDES ABSORPTION COLUMN (F-8 COLUMN)

K.L. Shanahan and S.F. Peterson

August 1989

WSRC-RP-89-786

INTRODUCTION

Large quantities of oxides of nitrogen (NOx) are routinely emitted from the F-Canyon dissolvers and from the F-Area A-Line denitrators. These gases are routed through a nitrogen oxides absorption column located in the A-Line. This column, referred to as the F-8 Column, removes NOx from the offgas streams of the dissolvers and denitrators and generates nitric acid. The nitric acid is recycled to the canyon dissolvers.

Because of continually more stringent environmental emission restrictions, control of the F-8 Column has become increasingly more difficult. The Savannah River Site has initiated a project to improve operation and control of the column. The project objectives are to use improved control to produce 50 (weight) percent nitric acid while limiting the instaneous NOx emission rate to maintain opacity from the F-Area stack to less than 40 percent. (A further goal is to reduce the yearly average NOx emissions to less than 20 pounds per hour.)

The Analytical Development Section (ADS) of the Savannah River Laboratory is supporting the A-Line NOx Absorption Column Improvement Project by determining how the column is currently performing and recommending ways to meet the project goals.

ADS chartered a Task Team to collect and study F-8 Column performance data and to recommend appropriate process control strategies. The Task Team constructed and installed an instrumentation package on the F-8 column which would record normal performance data. Simultaneously, an effort was mounted to construct a computer model of the column which would be used to test candidate process control strategies prior to actual Plant testing. This report describes that model. (A subsequent report will describe the instrumentation, model applications, and Plant tests.)

SUMMARY

Two versions of a FORTRAN computer model of the F-8 column were constructed. The first used internal code to calculate feed flows and compositions while the second read data files for that information. The second version was used to verify model performance relative to the real world and the first will be used to test process control strategies.

The model mimicked F-8 behavior sufficiently well that it could be used to screen process control strategies. When the model was run on the VAX 8550 and no other users were present, 36 hour dissolver runs were simulated in 5 minutes. The same model was run on a MicroVax II with simulation times of 30 minutes.

The model is highly empirical and contains severe approximations and assumptions. Some of these are:

- Minor chemical reactions are ignored.
- Rate constants, equilibrium constants, and reaction extents are empirically adjusted.
- Differential expressions are either integrated or approximated.
- Flows do not experience any holdups.
- Isothermality (mass balance only, no heat balance)

Each of these limitations is discussed below. A documented listing of the model is given in the Appendix.

The model will be used to screen process control strategies and the best candidate(s) will be then be tested in the Plant. Upon successful completion of this project, the results will be transmitted to the appropriate Plant personnel for inclusion in the final process control strategy implemented by the Plant.

PROCESS BACKGROUND

The F-8 column is a 44 tray bubble cap column 6 feet in diameter and 60 feet tall. Liquid capacity of the column is estimated at a minimum of 23 gallons per tray (1012 gallons total), with an additional 200 gallons in place during operation. The extra liquid produces a normal differential pressure (DP) across the column of 20" H_2O. Inlet pressure is nominally 6 psig. Gas flow is derived from two sources that are combined just before entering the column. The major sources of nitrogen oxides (NOx) are the 6.1 or 6.4 dissolver, which produce offgas composed of up to 70-80% NOx at approximately 400 scfm. The second source of NOx gases is the A-Line denitrators, which produce 0-10% NOx at approximately 700 scfm. A schematic diagram of the column is shown in Figure 1. Data collection points are indicated in the Figure by the circles.

Normal column operation when only the denitrators are functioning consists of allowing the denitrator offgas to flow through the F-8 column when the minimum volume of liquid is present. No acid is produced then, except on the trays themselves, and no emission problems have been tied to this type of operation. When the dissolver is operating however, additional water is sent to the column to capture the extra NOx and make concentrated nitric acid. Emission problems have been experienced during dissolver operations and weak acid is often produced.

A complete Purex dissolver run will take approximately 60 hours. The dissolutions are manually operated batch processes and show the typical type of variability that would be expected. In addition, the operation of the F-8 column is also manual, with the exception of a flow controller on the inlet water feed line, and also shows manual operation variability.

There are two main chemical operations in the reactor fuel dissolution process: removal of the aluminum cladding with sodium hydroxide, and dissolution of the uranium fuel with nitric acid. The declad fuel is heated in 50% acid, dissolving the uranium and fission products. The acid dissolution is accomplished in two separate steps, called cuts, each of which can take 10 to 14 hours to complete. The two cuts are normally separated by 2 to 5 hours, during which time the dissolved metal solution is removed and sent on for further processing and fresh acid is added.

Standard operating procedures call for the F-8 column operators to use a fixed water flow profile in all cases unless emission problems are encountered. The prescribed water flow profile is: 1.3 gallons per minute (GPM) for the first hour of the cut, 2.2 GPM for the next five hours, and 1.8 GPM for the remainder of the cut. If emissions problems are experienced the operators increase the water flow arbitrarily in an attempt to control emissions. In addition, prior to each cut, the operators attempt to develop the normal 20" H2O operating DP by adding water to the column at or near the maximum rate of 4 GPM until the desired DP is reached (usually 1/2 to 2 hours). Of four monitored dissolver runs, none used the prescribed profile exclusively.

PROCESS CONTROL PROBLEM

Fundamentally, each run will be slightly different due to differences in amount of fuel added to the dissolvers, random temperature variations, etc. However, to obtain exactly 50% acid, an exact amount of water must be used. The fixed flow profile strategy then is doomed to consistent failure on either the acid strength goal or the emissions level goal. The process control problem thus becomes how to determine the correct amount of water necessary and how to add it so that emissions are always at acceptable levels.

The problem is an inherently difficult one. Current data suggests that the NOx emission level at the top of the F-8 column averages near 1% by volume at a flow of perhaps 1000 scfm. F-8 emissions are mixed with filtered canyon emissions before atmospheric release and typical canyon air flows are 180,000 scfm. Thus the NOx emissions are diluted to near .0055 volume percent or approximately 60 ppm by volume.

In practice, emission control is accomplished by increasing the water flow and washing out the NOx more completely. However this adds additional water to the column and produces weak acid. The optimal process control strategy would hold the emissions at the maximum acceptable level while producing acid of the appropriate strength, barring any thermodynamic limitations on acid strength.

It should be obvious that trying to determine the optimal process control strategy via real-world testing would be both cost and time prohibitive. Computer modeling becomes the only viable rapid way to screen options. This is the justification of the ADD modeling effort, and it in turn places some minimum requirements on the model so developed. Most importantly, the model should mimic F-8 column behavior when varying NOx feeds are sent to it. Secondarily, the model should run somewhat faster than at real-time speeds.

This report describes an empirical first attempt at an F-8 computer model. The model assumptions are described and calculations based on real data are compared to actual performance. Limitations of the model are discussed and a path forward to an improved version of the model is outlined.

MODEL DESCRIPTION

Background

The F-8 computer model began as an attempt to maintain first-principles accuracy while minimizing software development time. A results-oriented emphasis was desired. Because of such considerations, simplification of first-principle models was required. The resultant model became essentially fully empirical and therefore modeling outside normal operating conditions should be considered highly suspect. In fact, oversimplification causes any results of this model to be suspect and requires all conclusions be verified by real world testing. However even with this caveat, the model does remarkably well at predicting column performance features from real data.

Several important assumptions were made in constructing the model. They are:

- Minor chemical reactions are ignored.
- Rate constants, equilibrium constants, and reaction extents are empirically adjusted.
- Differential expressions are either integrated or approximated

in a first order fashion.
- Flows do not experience any holdups.
- Isothermality (mass balance only, no heat balance)

Each of these, as well as some more subtle approximations, will now be discussed more fully.

Chemical Reactions and Rate, Equilibrium, and Mass Transfer Constants

Steady-state computer models of nitrogen oxides absorption columns abound as this process is a major way of producing concentrated nitric acid (1, Chilton). These models simulate the chemistry of several nitrogen species, such as NO, NO_2, N_2O_3, and N_2O_4, all being present in the gas and liquid phases. Mass transfer coefficients, equilibrium constants, and rate constants are thus necessary for all possible reactions. A good overview of this is given by Counce (2).

The calculational complexity of these models makes them inherently difficult to use in a dynamic sense, especially when rapid modeling turnaround is desired. Thus the chemistry normally included in column models was here simplified to include only four chemical reactions which are:

(1) $N_2O_4\ (g) \rightarrow N_2O_4\ (l)$

(2) $N_2O_4\ (l) + 1/2\ H_2O\ (l) \rightarrow 4/3\ HNO_3\ (l) + 2/3\ NO\ (g)$

(3) $NO\ (g) + 1/2\ O_2\ (g) \rightarrow NO_2\ (g)$

(4) $2\ NO_2\ (g) \longleftrightarrow N_2O_4\ (g)$

The first equation represents the net mass transfer of nitrogen species from the gas phase to the liquid phase. Real data show an approximately constant reduction in NOx concentration between feed and offgas concentrations. This suggested a fixed plate efficiency was required for accurate modeling. Steady-state models use this formalism as well. However, thermodynamic limitations do exist and are typically included via an equilibrium state calculation. When this standard method was tried, oscillatory behavior was encountered. Therefore an empirical approximation was used.

Instead of the more correct equilibrium calculations, an empirical approach to the limitations was used. This approach consisted of a variable plate efficiency where either a low and fixed efficiency was used when far from equilibrium levels or a smaller, smoothly decreasing plate efficiency was used when near to thermodynamic limits. The maximum plate efficiency was fixed at .075 for a time step of .05 minutes. The variable plate efficiency expression was given by:

$$\text{Plate Efficiency} = 10*t*\{\exp[-.025*(\text{acid weight percent})] - \exp[-.025*65\%\ ]\}$$

where t is the time step. This decreasing plate efficiency was caused to go to zero at 65% acid by subtracting its value at 65%. The multiplicative factor (-.025) inside the exponential term was empirically determined. Changes of 50 to 100% in this term substantially affected the ultimate acid strength obtained when testing process control strategies. Usually the real runs did not approach acid concentrations where the form of the approximation mattered, thus the actual value and form of this approximation cannot be tested.

The second chemical equation was assumed to go to completion.

The third chemical equation represents the rate-limiting gas phase equation. The model uses an integrated expression taken from Chilton (1) that calculates the fraction of NO oxidized based on initial NO and O2 partial pressures. The Chilton expression for the rate constant was used, although there are several others available. The calculated extent of oxidation never seemed correct however, and empirical corrections were applied to the rate constant and the fraction oxidized. The quadratic expression in fraction oxidized was solved via the quadratic formula and the positive root was shown to give unreal solutions, thus only the negative root is calculated in the model.

The Chilton reference was later found to have a typographical error in the integrated expression that transformed it from a quadratic in fraction oxidized to a cubic. This was not corrected in the model as an empirical fit had been obtained. Perhaps one of the cubic roots would have more accurately calculated the fraction NO oxidized.

The fourth chemical equation was assumed to be a fast equilibrium. The equilibrium constant expression was taken from Miller (3) and was not modified. The quadratic equilibrium expression in pressure was solved via the quadratic formula and the positive root was shown to always require more NO2 than was available. Thus only the negative root was used in the model.

The order in which the equations are listed represents the calculational order used in the model as well. Prior to calculating the chemical reactions, gas flow was simulated, and after the chemistry, liquid flow was simulated.

Gas and Liquid Flow

Gas and liquid flow expressions were extremely simplistic. For the liquid, flow onto a tray usually produced an equivalent off-flow. It was found necessary to limit off-flow to a maximum of 2.5 GPM to match a breakpoint in the acid concentration curves however.

Maximum tray liquid volumes were fixed by an assumed linear distribution of the nominal 20" of water differential pressure. Varying the amount and distribution of water on the column within the limits of normal operating differential pressure did not affect the results greatly.

Liquid flow is normally expressed as a differential equation. This implies a holdup time which is characterized by a time constant. The F-8 model assumes this constant to be zero under normal flow conditions. The model also uses a fixed operating differential pressure. The inclusion of differential equations into the model would allow these restrictions to be dropped, but this would also require the determination of the column time constant.

To simulate gas flow a linear pressure profile across the column that distributed the 20" of water differential pressure equally on each tray was assumed. Then the amount of gas injected onto the column in one time step was calculated and added to the gas space above tray 1. A pressure was calculated from this and compared to the 'ideal' pressure and any excess gas was moved up to the next tray. This was repeated for all trays. Next, the chemistry calculations were done, followed by the liquid flow. If enough NOx was present and moved to the liquid phase, gas flow could potentially be precluded in the next time step. In practice this never occurred when conditions approximating real ones were simulated.

The minimum liquid tray volume was set at 23 gallons and the tray gas volume was set at 35.34 cubic feet. The use of the 20" of excess water during operation was not accounted for in the gas volume which is a hidden approximation.

The bottom of the column has an approximate capacity of 360 gallons. This volume serves to hold up changes in product acid concentration. The flow out of the column bottom is controlled by a level controller changing a valve opening. In simulations, it was found that an assumed volume of 180 gallons reproduced actual measured data reasonably well.

Isothermality

The F-8 column uses dual cooling coils in the bottom 22 trays and single coils in the upper half. Chilled process water is fed at the bottom of the column and the cooling water takeoff is also there. An appropriate analogy is a ladder with flow in at the bottom of the left leg and flow out at the bottom of the right. No flow monitors are available to measure cooling water flow in the coils and worries about whether any flow occurs in the top coils are valid. No temperature information was available for incoming water temperature or tray temperatures, so the determination of actual heat transfer characteristics was impossible. These complications led to the decision to build a model based solely on mass balance.

While the oxidation rate constant and the equilibrium constant contained temperature dependence, the mass transfer coefficient did not. Also the second chemical reaction was assumed to go to completion. Thus temperature effects were not explicitly included in two of the four chemical reactions. Actual field data showed product acid temperature variations of 15 to 20 degrees Centigrade. Therefore the isothermality assumption may also be severe, at least for the lowest few trays.

Initial Conditions

The initial conditions used to start a simulation are always critical. This model used the following assumptions:

- 79% N2 and 21% O2 gas composition
- Gas pressure in each tray given by a linear decrease in pressure from the inlet pressure of 1.4 atm. totaling 20" of water (.05 atm.)
- Liquid volume on each tray equal to 23 gallons plus the linearly distributed excess volume equivalent to 20" of water.
- Acid on trays 1 to 12. Trays 1, 2, and 3 would have the same concentration with subsequent tray concentrations decreasing linearly to zero at Tray 13. Actual concentration on Tray 1 was determined by either matching real data initial product acid concentration or choosing an appropriate value for simulated feeds.
- Column bottom acid equal to Tray 1 acid concentration.

Other Assumptions

Other implicit and explicit assumptions include:

- No reactions occur in pipes.
- Complete mixing in gas and liquid phases.
- Remaining gas volume are made up by air (79% N2 / 21% O2).
- No other gases are present.

Model Verification

In the context of the F-8 model, verification means the process whereby the model was shown to simulate F-8 behavior within the limits required to accomplish the ADS program objectives. This was done by feeding the computer program real data collected via the F-8 instrumentation package and modifying both the model and the data until acceptable results were obtained.

At the time of writing this report, data covering 15 runs had been collected. However, most of these were incomplete due to instrument malfunction and/or the fact that a particular sensor's output was not added into the data acquisition system until later. In some cases these lacks could be made up from information from run patrol records, but these sheets were not always available and in at least one case disagreed with information on the run DPSOL. In addition, actual denitrator and product acid flow sensors were not present. Of the 15 runs only two were deemed suitable for direct modeling (if denitrator and water flow rates to the column could be correctly assumed). The rest had one or more of a variety of problems that disqualified them except for use in formulating an 'average' composite run.

Only in a few of later dissolver runs was water flow to the column logged by the data acquisition system, thus in the majority of the modeling the prescribed water flow profile was used. Of four runs with logged water flows available at the writing of this report, none used the prescribed water flow profile exclusively.

Data manipulation was found to be necessary to make the model act like the F-8 column. Approximate mass balance calculations on the raw data showed disagreements of up to 35% of the incoming material. This fact suggested potential absolute calibration errors in flows, as the NOx, acid, and O2 monitors were externally calibrated with recognized standards and methods.

As no flow sensor was available for the denitrator flow rate, the denitrator flows were back-calculated by subtracting the dissolver flow from the offgas flow and then adding flow for the absorbed dissolver NOx (absorption would cause a drop in offgas flow). This was an approximation as no correction for denitrator stream NOx content was possible.

When the actual dissolver flow and composition profiles, the actual denitrator composition profile, the estimated denitrator flow profile, and the assumed or actual water flow profile were used as input for the model, high emissions were calculated when acid concentrations approached those actually observed. This implied more NOx was being sent to the model than actually occurred in the real run. Only by reducing dissolver and denitrator flows could both emission and acid composition profiles be approximated.

It was also noted that without the flow adjustment, the offgas oxygen compositions were initially much different than actually observed. The matching of the calculated offgas oxygen volume percent to that observed was used as the indicator for the amount of flow rate adjustment needed. This was accomplished by decreasing denitrator flow as well as adjusting dissolver flow. Matching of acid composition and offgas NOx composition was then optimized by adjustment of parameters inside the F-8 computer model itself.

In some cases, the actual runs had emission problems and the operators would respond by increasing water flow rates. Whenever this was recognized from run patrol sheets or operator notes on the run DPSOL, the water flow rate fed to the model was adjusted appropriately. Additionally, it is a common practice to begin a run with less than 20" H2O DP on the column, and to add additional water between the cuts to maintain the DP. Further, manual override of the flow controller on product acid is possible, and has been suggested to happen on occasion.

Thus the overall verification process consisted of (1) selecting 'modelable' runs (a judgment decision which attempted to balance data problems with modeling results), (2) determining the extent the real data had to be adjusted, and (3) comparing the calculated output profiles with observed column data.

Two runs were selected as primary candidates for the verification effort. They were the dissolver runs of July 10, 1988 and July 25, 1988. Figures 2, 3, 4, 5, and 6 show the actual data collected from the July 10 run. The NO2 profiles are presented in Fig. 2, the NO profiles in Fig. 3, gas flows in Fig. 4, acid composition in Fig. 5, and O2 composition and feed water flow profiles in Fig. 6. Similar plots are shown for the July 25 run in Figures 7 to 11. The O2 sensor was beginning to malfunction during the July 10 run (indicated by the abrupt shifts in baseline seen in Figure 5) and had failed completely during the July 25 run, therefore no O2 profile is shown in Figure 11.

The July 10 run appeared to be a normal run. Note however that the feed water flow profile still shows divergences from the procedural profile. Specifically, flow did not go to zero at the end of the first cut and the high flow region of the second cut extends for more than 5 hours.

The July 25 run experienced emission problems. Apparently the operators did not recognize or were not notified of the start of the second cut. They did not adjust the water flow at the start of the second cut and did not notice this until the cut was almost complete. This particular run is perhaps one of the most severe tests possible for the model because the differential pressure across the column would have dropped significantly during the second cut. This would severely test the empiricisms of the model.

Figures 12 to 17 present the 'best' simulation results of these two runs. The actual data are shown as solid or dashed lines while the simulations are shown as dotted lines.

Both simulations used the same model parameters. The only differences were in the initial acid concentration profile on the column trays and the actual data sets used. Table 1 lists the initial tray concentration profiles used. In practice the only important feature of these profiles was the need to make trays 1 through 3 have the same concentration as the column bottoms. This prevented an immediate dip in product acid concentration at the start of the simulation.

Table 1.
F-8 Column Tray Nitric Acid Concentration Initial Conditions (Weight Percent)

	July 10, 1988 Run	July 25, 1988 Run
Column Bottom		
Tray 1	38	39
Tray 2	38	39
Tray 3	38	39
Tray 4	34.5	33.5
Tray 5	31	28.5
Tray 6	26	23.5
Tray 7	21	19.5
Tray 8	15.5	15.5
Tray 9	11	11
Tray 10	5	5
Tray 11	1.5	1.5
Tray 12	1	1
Tray 13	1	1

Tray 14 to 44 all set to 0% acid

The most severe failure of the model in exactly matching the actual data is with regards to the acid composition profiles. Unexplained dips are present, and both simulations seem to lag the real data. However, the purpose was not to fit the data, but to mimic it within limits sufficient to determine the effects of process control strategies.

This is illustrated in Figure 18, here an additional simulation has been conducted on the July 10 run. In this simulation, a water flow control strategy based on feed forward techniques was used. Specifically, a theoretical equation relating the NOx feed to water addition under the assumptions that all NOx would be absorbed and 50 weight percent acid would be produced was used to calculate water flow to the column. No emission control strategy was employed here, but a restriction of water flow if acid strength was less than 40% was employed.

Obviously, the feed forward strategy has radically altered the profile. Compared to the change in profile, the mis-match of the simulation to the data becomes secondary. Similar effects are seen in the NOx emission profiles when emission control strategies are tested.

In conclusion, the modeling program goal was to quickly build a computer model of the F-8 column and use it to screen candidate process control strategies. The model described in this report satisfies that goal.

FUTURE PROGRAM

The F-8 computer model will be used to test process control strategies and hardware modifications such as weak acid recycle. The model's accuracy is not sufficient to allow blind acceptance of calculational results and therefore Plant testing of optimal process control strategies will be conducted. Upon successful completion of the Plant tests, the documented results will be transmitted to the appropriate Plant personnel for inclusion in the final process control strategy implemented by the Plant.

Barring unforeseen difficulties, no further work on refining the F-8 model is planned. If Plant tests do not bear out the general accuracy of the model, model refinements may be necessary. In anticipation of this (and other potential modeling applications), the DYFLO software package written by R. G. E. Franks of the DuPont Engineering Department has been obtained. This package approaches dynamic modeling from a more correct viewpoint than the current F-8 model and thus may serve as a base for an improved F-8 model.

References

1. "The Manufacture of Nitric Acid by the Oxidation of Ammonia" Thomas H. Chilton, Chemical Engineering Progress Monograph Series, Vol. 56, No. 3 American Institute of Chemical Engineers, 1960

2. "The Scrubbing of Gaseous Nitrogen Oxides in Packed Towers" Robert M. Counce, Oak Ridge National Laboratory Report No. ORNL-5676, 1980

3. "Nitric Acid Absorption" Donald N. Miller, DuPont Accession Report No. 17191, 1986

APPENDIX

Documented FORTRAN code

```
C       PROGRAM READER - A Simulation of the A-line Nitrogen Oxides
C                          Absorption Column (The F8 Column)
C               Kirk L. Shanahan   April 15, 1989
C
C
C       Documentation convention used herein is comments explaining code
C       will follow lines in question
C
C
C       This program simulates the F8 column. It reads external data files
C       originating from RS/1 tables written to files. The RS/1 tables are
C       derived from data files created on an IBM industrial PC which served
C       as a data logger to an instrumentation package consisting of a Dupont
C       NOx analyzer, two acid concentration and temperature measurers (a
C       densitometer and a refractometer), and an electrochemical oxygen
C       analyzer. Also logged were dissolver and offgas line gas flow rates
C       and column water addition flow rates from preexisting sensors.
C
C       The input data file contains dissolver and denitrator NO2 and NO
C       concentrations, flow rates, and associated times (the data are
C       collected once every 15 minutes and the dissolver and denitrator
C       data are offset in time by 5 minutes), and column water input
C       addition rates. The units are volume percent, scfm, hours, and
C       gallons/minute. The data file is named INPUT.DAT.
C
C       The input data is read in and stored in arrays. The program linearly
C       interpolates from point to point to the desired time step resolution.
C
C       This program also includes code to simulate the effects of a recycle
C       stream fed to Tray 11 of the 44 tray column.
C
C       Pressures are calculated in atmospheres, volumes in gallons,
C       temperatures in degrees Centigrade, flows in cubic feet/minute,
C       time is usually in minutes, except for output purposes where it
C       has been converted to hours.
C
C       The ideal gas law is used throughout. Linearized behavior is used
C       throughout.
C
C  DATA TYPE AND ARRAY DECLARATION SECTION
C
      REAL TIME1(250), FLOW1(250), NO2_1(250), NO_1(250)
      REAL TIME2(250), FLOW2(250), NO2_2(250), NO_2(250)
      REAL WATERIN(250), MAXTIME
C
C       These arrays hold the input data. Subscript 1 => Dissolver
C       Subscript 2 => Denitrator values.
C       MAXTIME is the last time assosiated with the dissolver data.
C       It is used to shut down the program when the data runs out.
C
      REAL VOLUME(44)
      REAL NO(44),NO2(44),N2O4(44),N2(44),O2(44),HNO3(44)
      REAL PNO(44),PNO2(44),PN2O4(44),PN2(44),PO2(44)
      REAL FNO(44),FNO2(44),FN2O4(44),FN2(44),FO2(44),FHNO3(44)
C
C       These arrays hold the values for the actual tray volume (VOLUME) in
C       gallons, moles of gas at each tray (NO, NO2, N2O4, N2, O2), partial
C       pressure of each gas at each tray (PNO, PNO2, PN2O4, PN2, PO2) in atms.,
C       mole fractions of each gas at each tray (FNO, FNO2, FN2O4, FN2, FO2),
```

```
C        moles of HNO3 in the liquid on each tray (HNO3), and the concentration
C        of HNO3 at each tray (FHNO3) in moles/gallon.
C
C        The mole fraction arrays are superfluous here, but were retained
C        for consistency with the FORTH/ACA 32000 version of this model.
C        Partial pressures are used in some calculations, but the arrays
C        could be made superfluous by calculating partial pressures when
C        needed.
C
      REAL FULLVOL(44), PRESSURE(44)
C
C        FULLVOL holds the 'nominal' full tray volume in gallons. This
C        volume is calculated later by assuming an operating differential
C        pressure across the column. This is normally 20" of water. This
C        excess of water is distributed in a linearly decreasing fashion
C        across the column. This pattern is an assumtion. Liquid flow is
C        accomplised in this model by moving out the excess volume over
C        that specified by FULLVOL, plus a trickle rate, up to a maximum flow
C        rate. This is an assumption.
C
C        PRESSURE holds the 'nominal' pressure at each tray. The nominal
C        values are calculated by assuming a linear pressure profile across
C        the column between the inlet and outlet pressures. Gas flow is
C        accomplished in this model by comparing moles of gas actually
C        present to the ideal, calculated from the PRESSURE numbers, and
C        moving any excess up the column.
C
      REAL INLET,OUTLET
C
C        INLET and OUTLET are the inlet and outlet pressure of the column.
C        The inlet pressure is determined by the denitrator and dissolver
C        pumps and is assumed to be a constant 6 psig or approx. 1.4 atms.
C        The outlet pressure is assumed to be 20" of water less, or
C        approx. 1.35 atm.
C        These values are set later by coded statements.
C
      REAL NEXTTIME1, NEXTTIME2, NEXTDISNO2, NEXTDISNO, NEXTWATERIN
      REAL NEXTDENNO2, NEXTDENNO, NEXTDISFLOW, NEXTDENFLOW
C
C        These values hold data from the data arrays that is used in the
C        interpolations. They are matched by a set of variables where NEXT
C        is replaced by FIRST. Again, 1 and 2 imply dissolver and denitrator,
C        repectively. DEN means denitrator, DIS means dissolver.
C
      REAL N2X,O2X,NOX,NO2X,N2O4X
C
C        Thses variables hold the moles of each offgas at each step.
C
      REAL N2OUT,O2OUT,NOOUT,NO2OUT,N2O4OUT,HNO3OUT
C
C        These variables hold the times averages of the offgas moles and
C        product acid weight percent. Current time base for the average
C        is one minute. These variables are written to the results file,
C        RECYCLE.DOC
C
      DIMENSION FACTOR(4)
      DATA FACTOR/2.5,5.0,4.0,5.0/
C
C        The FACTOR array is used to store flow correction factors when
```

```
C       multiple simulations are conducted with one program run.
C END OF DECLARATION STATEMENTS
C
      DO MASTER = 1, 1
C
C       The MASTER DO loop is used for multiple simulations. Here it
C       is set for 1 simulation only. Setting the final index higher
C       will give that many runs with different flow correction
C       factors, up to the dimensioned limit of 4.
C

      OPEN(UNIT=19,FILE='INPUT.DAT',FORM='FORMATTED',STATUS='OLD')
      READ (19,*) LOOPS
C
C       This is a free-formatted READ statement. It only requires the data
C       in the data file be separated by spaces. LOOPS is an integer in
C       the first line of the data file that tells the program the
C       actual number of data lines.
C
      DO M = 1, LOOPS
      READ (19,*) TIME1(M),NO2_1(M),NO_1(M),FLOW1(M),TIME2(M),
     + NO2_2(M),NO_2(M),FLOW2(M),WATERIN(M)
      END DO
      CLOSE(UNIT=19)
C
C       This section of code reads the data file (on Unit 19) and stores
C       the numbers in the data arrays. Current maximum size is 250 lines
C       of data. A free-formatted READ is used here also.
C
C       For simulated (calculated) data, the data file should contain the
C       artificial data.
C
C

      OPEN(UNIT=3,FILE='RECYCLE.DOC',FORM='FORMATTED',STATUS='NEW')
C
C       This statement opens the results file.
C
C
C  INITIALIZATION SECTION
C
      FXHNO3=0.
C
C       A variable that is used to hold product acid weight percent (and
C       related intermediate values) and which is averaged for output.
C
      TIMESTEP=.05
C
C       The program timestep in minutes.
C
      FCOUNT=1./TIMESTEP
      MAXCOUNT=INT(FCOUNT)
      MINUTE = 0
      LOOPCOUNT=0
C
C       Numbers needed to control the output and associated averaging.
C
      VOLMIN = 23.
C
C       The assumed minimum residual tray volume in gallons. This volume
```

```
C       is always present in each tray.
C
      TRICKLEMAX = .70
      TRICKLEVOL= TRICKLEMAX * TIMESTEP
C
C       The assumed column drain rate and drain volume per step.
C
      MAXTIME=TIME1(LOOPS)
C
C       This limits the number of program steps when using real data.
C       It should be disabled when using simulated data. The progam stop
C       point should be controlled via the STEP variable directly below.
C
      STEP=42000
C
C       The main program loop index. If working from real data, this number
C       should be bypassed via MAXTIME unless its too small. If using
C       simulated data it will be the number of steps through the program.
C
      T=303.
C
C       This model is isothermal, perhaps a severe assumption. T is the
C       assumed temperature in degrees Centigrade.
C
      INLET=1.4
      OUTLET=1.35
      SLOPE= (INLET-OUTLET)/43.
C
C       The inlet and oulet pressures. SLOPE is used below to calculate
C       the tray 'nominal' pressure (PRESSURE).
C
      COLVOLUME = 180.
      COLMOLES = COLVOLUME * 30.
C
C       The bottom of the column serves as a small hold tank. The volume
C       of 180 gallons is assumed. The concentration is set here to
C       30 moles/gallon initially, and the moles in the column bottom
C       calculated.
C
      FHNO3(1)=30.
      FHNO3(2)=30.
      FHNO3(3)=30.
      FHNO3(4)=27.
      FHNO3(5)=24.
      FHNO3(6)=21.
      FHNO3(7)=18.
      FHNO3(8)=15.
      FHNO3(9)=12.
      FHNO3(10)=9.
      FHNO3(11)=6.
      FHNO3(12)=3.
      FHNO3(13)=1.
      DO 1111 I= 14,44
 1111 FHNO3(I)=0.
C
C       The column usually has residual acid on it. The values here are in
C       moles/gallon and assume a linearly decreasing profile. This particular
C       set of values was chosen to match a set of real data. Each set of real
C       data requires a different set of assumed concentrations here.
```

```
C
      DO 100 I=1,44
C
C       This DO loop initializes the other arrays. The column is assumed to
C       start with air as the gas (21% O2) and 20" of water differential
C       pressure.
C
C      FULLVOL(I)=17.62555766*(-.014061655*XI+.618713)+VOLMIN
C
C       This line of code was used to give 13" of water DP on the column.
C       (Some real runs were started with 13" DP.)
C
      XI=FLOAT(I)
      PRESSURE(I)=(44.-XI)*SLOPE+OUTLET
C
C       This line produces the linear pressure profile across the column.
C
      FULLVOL(I)=17.62555766*(-.021633315*XI+.951865873)+VOLMIN
      VOLUME(I)=FULLVOL(I)
C
C       These lines calculate the linear fluid volume profile and set
C       the initial volume to that 'ideal' volume.
C
      N2(I)=.79*PRESSURE(I)*35.34 /(.00289778*T)
      O2(I)=.21*PRESSURE(I)*35.34 /(.00289778*T)
      NO(I)=0.
      NO2(I)=0.
      N2O4(I)=0.
      HNO3(I)= FHNO3(I) * VOLUME(I)
C
C       These lines fill the mole arrays with initial values.
C
      PN2(I)=.79*PRESSURE(I)
      PO2(I)=.21*PRESSURE(I)
      PNO2(I)=0.
      PNO(I)=0.
      PN2O4(I)=0.
C
C       These lines fill the pressure arrays with initial values.
C
      FNO(I)=0.
      FN2O4(I)=0.
      FNO2(I)=0.
      FN2(I)=.79
 100  FO2(I)=.21
C
C       These lines fill the mole/weight fraction arrays with initial
C       values.
C
      WATER=.5
C
C       WATER is the 'nominal' column water flow rate in gallons/minute.
C       When recycle is simulated the recycle flow rate and the water addition
C       rate at the top of the column add to equal WATER.
C
C END OF INITIALIZATION SECTION
C
C  SET UP DATA INTERPOLATION
C
```

```
      M1 = 2
      M2 = 2
C
C       Indicies used to remember the last data line used for interpolation.
C       The dissolver and denitrator interpolations are not coupled.
C       By using MAXTIME based on the dissolver times, M2 should lag M1, if
C       they are not equal.
C
C   FIRST LINE OF DATA MUST HAVE ETIMES OF ZERO!!!
C
      FIRSTTIME1 = TIME1(1)
      NEXTTIME1 = TIME1(2)
      FIRSTDISNO2 = NO2_1(1)
      NEXTDISNO2 = NO2_1(2)
      FIRSTDISNO = NO_1(1)
      NEXTDISNO = NO_1(2)
      FIRSTDISFLOW = FLOW1(1)
      NEXTDISFLOW = FLOW1(2)
      FIRSTTIME2 = TIME2(1)
      NEXTTIME2 = TIME2(2)
      FIRSTDENNO2 = NO2_2(1)
      NEXTDENNO2 = NO2_2(2)
      FIRSTDENNO = NO_2(1)
      NEXTDENNO = NO_2(2)
      FIRSTDENFLOW = FLOW2(1)
      NEXTDENFLOW = FLOW2(2)
      FIRSTWATERIN = WATERIN(1)
      NEXTWATERIN = WATERIN(2)
      DELTIME1 = TIME1(2) - TIME1(1)
      DELTIME2 = TIME2(2) - TIME2(1)
      DELDISNO2 = NO2_1(2) - NO2_1(1)
      DELDISNO = NO_1(2) - NO_1(1)
      DELDENNO2 = NO2_2(2) - NO2_2(1)
      DELDENNO = NO_2(2) - NO_2(1)
      DELDISFLOW = FLOW1(2) - FLOW1(1)
      DELDENFLOW = FLOW2(2) - FLOW2(1)
      DELWATERIN = WATERIN(2) - WATERIN(1)
C
C       The above quantities are the inital 'FIRST' and 'NEXT' sets of data
C       points used to start the interpolations. The 'DEL' quantities are
C       used in the interpolation calculation.
C
      DO 2000 II=1,STEP
      ETIME= (FLOAT(II))*TIMESTEP / 60.
      IF (ETIME .GT. MAXTIME ) GO TO 999
C
C       ETIME is the current simulation time in hours. When using real data
C       it is compared to MAXTIME to check for program end.
C
      IF (ETIME.GT.NEXTTIME1) THEN
C
C       This IF statement checks to see if the current time has exceeded the
C       interpolation range defined by FIRSTTIME1 and NEXTTIME1. If it does,
C       the oldest values are deleted and the next line of data is used.
C

                M1 = M1 + 1
                FIRSTTIME1 = NEXTTIME1
                NEXTTIME1 = TIME1(M1)
```

```
            FIRSTDISNO2 = NEXTDISNO2
            NEXTDISNO2 = NO2_1(M1)
            FIRSTDISNO = NEXTDISNO
            NEXTDISNO = NO_1(M1)
            FIRSTDISFLOW = NEXTDISFLOW
            NEXTDISFLOW = FLOW1(M1)
            FIRSTWATERIN = NEXTWATERIN
            NEXTWATERIN = WATERIN(M1)
            DELTIME1 = NEXTTIME1 - FIRSTTIME1
            DELDISNO2 = NEXTDISNO2 - FIRSTDISNO2
            DELDISNO = NEXTDISNO - FIRSTDISNO
            DELDISFLOW = NEXTDISFLOW - FIRSTDISFLOW
            DELWATERIN = NEXTWATERIN - FIRSTWATERIN
        END IF
C
C       Resets dissolver and water interpolation if ETIME exceeeds MAXTIME
C
      IF (ETIME.GT.NEXTTIME2) THEN
            M2 = M2 + 1
            FIRSTTIME2 = NEXTTIME2
            NEXTTIME2 = TIME2(M2)
            FIRSTDENNO2 = NEXTDENNO2
            NEXTDENNO2 = NO2_2(M2)
            FIRSTDENNO = NEXTDENNO
            NEXTDENNO = NO_2(M2)
            FIRSTDENFLOW = NEXTDENFLOW
            NEXTDENFLOW = FLOW2(M2)
            DELTIME2= NEXTTIME2 - FIRSTTIME2
            DELDENNO2 = NEXTDENNO2 - FIRSTDENNO2
            DELDENNO = NEXTDENNO - FIRSTDENNO
            DELDENFLOW = NEXTDENFLOW - FIRSTDENFLOW
        END IF
C
C       Resets denitrator interpolation if ETIME exceeeds MAXTIME
C
      DISNO2  =((DELDISNO2 *(ETIME-FIRSTTIME1))/DELTIME1)+FIRSTDISNO2
      DISNO   =((DELDISNO  *(ETIME-FIRSTTIME1))/DELTIME1)+FIRSTDISNO
      DISFLOW =((DELDISFLOW*(ETIME-FIRSTTIME1))/DELTIME1)+FIRSTDISFLOW
      WATER   =((DELWATERIN*(ETIME-FIRSTTIME1))/DELTIME1)+FIRSTWATERIN
      DENNO2  =((DELDENNO2 *(ETIME-FIRSTTIME2))/DELTIME2)+FIRSTDENNO2
      DENNO   =((DELDENNO  *(ETIME-FIRSTTIME2))/DELTIME2)+FIRSTDENNO
      DENFLOW =((DELDENFLOW*(ETIME-FIRSTTIME2))/DELTIME2)+FIRSTDENFLOW
C
C       These do the interpolation.
C
      DENFLOW=DENFLOW+183.
      FACTOR=2.75+3.*TIMESTEP*FLOAT(II)/32./60.
      DISFLOW=DISFLOW/FACTOR
C
C       The above statements were used to adjust flow rates for a match
C       of calculated and measured column outputs. This is pure guesswork.
C       It was driven by first roughly matching calculated offgas O2% to
C       measured, then attempting to make the peak shapes of NOx offgas
C       coincide. Other simulations of real data did not require the time
C       drift in the dissolver flow, but did require a linear offset.
C
      ADIS=DISFLOW*TIMESTEP*INLET/(.00289778*303.)
      ADEN=DENFLOW*TIMESTEP*INLET/(.00289778*303.)
C
```

```
C         ADIS and ADEN are the moles of gas flowing into the column from
C         the dissolver and denitrator during the current timestep.
C
      DISAIR=  (100.-DISNO-DISNO2) /100.
C
C         DISAIR is the fraction of air in the dissolver leg.
C
      DISN2=   .79*DISAIR
      DISO2=   .21*DISAIR
C
C         Fraction of O2 and N2 in the dissolver leg.
C
      DENAIR=  (100.-DENNO-DENNO2) /100.
      DENN2=   .79*DENAIR
      DENO2=   .21*DENAIR
C
C         Ditto for the denitrator leg.
C
      N2(1)=  N2(1)   + DISN2*ADIS + DENN2*ADEN
      O2(1)=  O2(1)   + DISO2*ADIS + DENO2*ADEN
      NO(1)=  NO(1)   + ADIS*(DISNO /100.)   + ADEN*(DENNO /100.)
      NO2(1)= NO2(1)  + ADIS*(DISNO2 /100.) + ADEN*(DENNO2 /100.)
C
C         This initiates the gas flow by adding moles of NOx and air to
C         tray 1 from the dissolver and denitrator, based on measured
C         NOx levels and assumed air concentrations.
C
      SUMINNOX= ADIS*(DISNO /100.)   + ADEN*(DENNO /100.)
     +          + ADIS*(DISNO2 /100.) + ADEN*(DENNO2 /100.)
C
C         SUMINNOX is the molar sum of NOx species entering the column.
C         It is used in the feedforward process control strategy.
C
      DO 200 I=1,43
      A=N2(I)+O2(I)+NO(I)+NO2(I)+N2O4(I)
      B=PRESSURE(I)*35.34/(.00289778*t)
C
C         This is the loop that moves the gas through the column. The actual
C         total moles present are calculated (A) and compared to the 'ideal'
C         moles for that tray (B) (based on the assumed pressure profile),
C         and any excess moles are transferred to the next tray.
C
      IF ((A-B) .LE. 0. ) THEN
                N2X=0.
                O2X=0.
                NOX=0.
                NO2X=0.
                N2O4X=0.
                IXXX=I
                GO TO 101
C
C         IF A is less than B, no excess moles are present and moles in the
C         offgas are set to zero. The 'X' subscripted variables are the moles
C         of that gas in the offgas for that timestep.
C         IXXX saves the loop counter to see if a calculation is needed for
C         tray 44 (if A is ever less than B, the calculation will not be
C         needed).
C
        ELSE
```

```
                A=(A-B)/A
C
C       Change A into the fraction of moles to be moved (when A>B).
C
                XX=A*N2(I)
                N2(I)=N2(I)-XX
                N2(I+1)=N2(I+1)+XX
                XX=A*O2(I)
                O2(I)=O2(I)-XX
                O2(I+1)=O2(I+1)+XX
                XX=A*NO(I)
                NO(I)=NO(I)-XX
                NO(I+1)=NO(I+1)+XX
                XX=A*NO2(I)
                NO2(I)=NO2(I)-XX
                NO2(I+1)=NO2(I+1)+XX
                XX=A*N2O4(I)
                N2O4(I)=N2O4(I)-XX
                N2O4(I+1)=N2O4(I+1)+XX
                IXXX=I
C
C       The number of moles of each gas to be moved is calculated by
C       multiplying the fraction of moles to be moved times each gas'
C       current mole total and stored in a dummy variable XX. XX is then
C       subtracted from the current tray and added to the next tray.
C       Again, the loop counter is stored in IXXX.
C
        END IF
  200 CONTINUE
  101 IF (IXXX.EQ.43) THEN
C
C       This IF duplicates the above section for tray 44 if needed,
C       but instead of adding to the next tray if flow is indicated,
C       it puts the excess moles into the offgas variables.
C
      A=N2(44)+O2(44)+NO(44)+NO2(44)+N2O4(44)
      I=44
      B=PRESSURE(I)*35.34/(.00289778*t)
      IF ((A-B) .LE. 0.) THEN
                N2X=0.
                O2X=0.
                NOX=0.
                NO2X=0.
                N2O4X=0.
        ELSE
                A=(A-B)/A
                N2X=A*N2(I)
                N2(I)=N2(I)-N2X
                O2X=A*O2(I)
                O2(I)=O2(I)-O2X
                NOX=A*NO(I)
                NO(I)=NO(I)-NOX
                NO2X=A*NO2(I)
                NO2(I)=NO2(I)-NO2X
                N2O4X=A*N2O4(I)
                N2O4(I)=N2O4(I)-N2O4X
        END IF
      END IF
C
```

```
C
C
C
C END OF GAS FLOW CALCULATIONS
C
C START OF CHEMISTRY CALCULATONS
C
      DO 300 I=44,1,-1
      SUMMOLES=NO(I)+N2O4(I)+NO2(I)
      IF (SUMMOLES.GT.0.) THEN
        NOXTRAY=I
        GO TO 111
      END IF
 300   CONTINUE
      NOXTRAY=0
 111      CONTINUE
C
C       The 300 loop locates the highest tray with NOx on it. Calculations
C       of NOx chemistry are only done for those trays below that point.
C
      DO 400 I=1,NOXTRAY
C
C       The next section calculates the amount of gaseous N2O4 moved to
C       the liquid phase. All of the liquid phase N2O4 is reacted to form
C       HNO3 acid and gaseous NO. The amount of N2O4 transferred is
C       calculated from an empirical formula similar to a plate efficiency,
C       except the efficiency depends in an exponential fashion on acid
C       weight percent on the tray. The -3.25 term pegs the coefficient
C       to zero at 65% acid.
C
               IF( VOLUME(I).GT.0. ) THEN
C
C       If there's no water on the tray, no acid can be formed.
C
               F=FHNO3(I)*.264172
               F= (.006025225*f**3-.205523*f**2+6.304383*f)
C
C       The empirical efficiency coefficient is based on weight percent
C       numbers, thus the acid concentration in moles/gallon has to be
C       converted to weight percent. A statistical fit derived from tables
C       in the CRC Handbook of Chemistry and Physics, 66th ed. is used.
C
               DEL= 10*TIMESTEP*(EXP( -.025*F)-EXP(-1.625))
               IF (DEL .GT. .075) DEL = .075
C
C       DEL is the empirical plate efficiency. It is fixed at .075 for
C       low acid concentrations and falls off exponetially at high
C       concentrations. This is an attempt to simulate the
C       thermodynamics. The subtractive term limits acid concentration to
C       65 wt.% by disallowing N2O4 mass transfer above that level.
C
               DEL = DEL * N2O4(I)
C
C       Converts DEL to the number of moles moved to the liquid phase.
C
               N2O4(I)=N2O4(I)-DEL
               HNO3(I)=HNO3(I)+DEL*4./3.
               NO(I)=NO(I)+DEL*2./3.
       ENDIF
```

```
C
C       The next section calculates the amount of NO oxidized to NO2.
C       The method used here was an attempt to use an integrated rate
C       expression published in "The Manufacture of Nitric Acid by the
C       Oxidation of Ammonia", Thomas H. Chilton, Chem. Eng. Progr.
C       Monograph Series, No. 3, Vol. 56, (1960), pg. 8. The equation,
C       a quadratic, was solved via the quadratic formula and it was found
C       that the positive root gave unreal solutions. Therefore only the
C       negative root was calculated here. Unfortunately, this still did
C       not produce good agreement with real data and an empirical correction
C       to the rate constant and the fraction oxidized was needed to reach
C       good agreemement. After this version was written it was discovered
C       that the published equation had an error where a power was dropped,
C       making the equation a cubic in fraction oxidized. This model version
C       does not attempt to correct this.
C
        XPO2 = O2(I) * 0.00289778 * T / 35.34
        XPNO = NO(I) * 0.00289778 * T / 35.34
C
C       Instantaneous oxygen and NO partial pressures.
C
        IF (XPNO .LT. 0.00001) XPNO = 0.0
C
C       The IF statement is an attempt to limit roundoff error, which may
C       or may not be present. In earlier versions, slight roundoff errors
C       had caused very small but negative numbers here, which caused
C       calculational problems.
C
      IF ( ( XPO2 .GT. 0.0 ) .AND. ( XPNO .GT. 0.0 ) ) THEN
C
C       If no O2 or NO, no reaction is possible, therfore bypass calculation.
C
        EQK3=10**(635./T + 1. )
C
C       One of the published rate equations (Chilton), with a
C       modified constant (published = -1.026).
C
        C = 2.0 * XPO2 / XPNO
        B = 0.5 * (C + 1.0 + (8.0 / ( EQK3 * TIMESTEP * XPNO**2 )))
        A = B - SQRT(B**2 - C)
      ELSE
        A = 0.
C
C       A is the fraction oxidized. B and C are dummy variables used in
C       solving the simplified quadratic formula used here.
C
      ENDIF
      A=.75*A*NO(I)
C
C       This converts A, the fraction oxidized, to A, the moles consumed.
C       The .75 is an empirical factor that affects the NO/NO2 ratio.
C       It may correct for the error in the formula in the text.
C
      IF (A.GT.NO(I) )  THEN A=NO(I)
      IF (.5*A.GT.O2(I)) THEN A=2.*O2(I)
C
C       Checks to make sure enough NO and O2 is prosent for the calculated
C       extent of reaction.
C
```

```
      NO(I)=NO(I)-A
      O2(I)=O2(I)-.5*A
      NO2(I)=NO2(I)+A
C
C       Adjust the gas moles appropriately.
C
C
C       The next section uses basic equlibrium chemistry to equlibrate
C       NO2 and N2O4. The equation is a quadratic, so the quadratic formula
C       is used here also. The positive root was found to always predict
C       consumption of twice the available NO2, therefore only the negative
C       root is calculated here.
C
      PN2O4(I)=N2O4(I)*.00289778*T/35.34
      PNO2(I)=NO2(I)*.00289778*T/35.34
C
C       Calculates the NO2 and N2O4 partial pressures.
C
      EQK4=EXP( 6893./T-21.247 )
C
C       One of the published equlibrium constants, D. N. Miller,
C       "Nitric Acid Absorption", E. I. DuPont Accession Report
C       No. 17191, August 1980.
C
      B=.125/EQK4 + .5*PNO2(I)
      C=.25*PNO2(I)**2 - .25*PN2O4(I)/EQK4
      A=B-SQRT( B**2-C )
C
C       Simplified solution to the quadratic equation. A is the N2O4
C       pressure change.
C
      A=A*35.34/(T*.00289778)
C
C       Convert A to the N2O4 moles change.
C
      N2O4(I)= A + N2O4(I)
      NO2(I)=NO2(I)- 2*A
C
C       Correct the NO2 and N2O4 moles accordingly.
C
 400  CONTINUE
C
C END OF CHEMISTRY CALCULATIONS
C
      IF (NOXTRAY.GT.0) THEN
      DO 600 I=1,44
      PN2(I)=N2(I)*.00289778*T/35.34
      PO2(I)=O2(I)*.00289778*T/35.34
      PNO(I)=NO(I)*.00289778*T/35.34
      PNO2(I)=NO2(I)*.00289778*T/35.34
      PN2O4(I)=N2O4(I)*.00289778*T/35.34
      F=N2(I)+O2(I)+NO(I)+NO2(i)+N2O4(i)
      FN2(i)=N2(i)/F
      FO2(i)=O2(i)/F
      FNO(i)=NO(i)/F
      FNO2(i)=NO2(i)/F
      FN2O4(i)=N2O4(i)/F
      IF (VOLUME(I).GT.0.) THEN
      FHNO3(I)=HNO3(I)/VOLUME(I)
```

```
      ELSE
      FHNO3(I)=0.
      ENDIF
 600  CONTINUE
C
C       The above section updates mole fraction and partial pressure arrays.
C
      ENDIF
C
C START OF LIQUID FLOW CALCULATIONS
C
C       The liquid flow calculation assumes (incorrectly) that flow out
C       of a tray equals flow onto it with no holdup. Thus water is added
C       at the top of the column, mixed on the first tray, and the excess
C       plus a trickle amount is moved down to the next tray. The excess
C       is determined by comparing the tray liquid volume with an 'ideal'
C       volume given by a linear distribution of the water required to
C       maintain the normal operating differential pressure of 20" of water.
C       This is an assumption that is usually incorrect. This assumption
C       makes it difficult to draw conclusions as to flow-related
C       characteristics within the column.
C
C     IF (MASTER .LT. 3) GO TO 888
C THE GOTO SKIPS THE WATER FEEDFORWARD AND FEEDBACK CONTROLS
C IT GENERATES A FORTRAN WARNING STATEMENT WHEN COMPILING AND LINKING
C
C       The IF is necessary only if multiple runs are done to compare
C       conditions with and without simulated process control.
C
C       The next section calculates the water flow to the column. This
C       version of the model uses a feedforward strategy based on the
C       NOx moles flowing into the column, a feedback strategy based
C       on the moles of NOx in the offgas, and a feedback strategy based
C       on the product acid weight percent.
C
      IF (FXHNO3 .GE. 40.) THEN
C
C       The acid weight percent feedback criterion, currently set to
C       limit water flow to prevent excessive dilution if acid weight
C       percent is less than 40%.
C
                WATER= .333*SUMINNOX
C
C       The constants were empirically determined. SUMINNOX is calculated
C       in the gas flow section.
C
                IF (WATER.GT.2.5) WATER=2.5
C
C       The water flow was limited to 2.5 gallons/minute maximum to limit
C       dilution effects.
C
        ELSE
                WATER=.4
C
C       When the product acid is weak, only enough water is added to
C       counterbalance the draining of the column. The .7 was derived by
C       fitting real data in the region between the cuts with this model.
C
                IF(SUMINNOX.LT. .5) WATER=0.
```

```
C
C       Assumes that if NOx in is low, such as between cuts, the water
C       should be turned off. (Depending on column differential pressure
C       it might be more appropriate to set the flow to .7 gal./min.)
C
        ENDIF
      SUMOUTNOX=100*( NO2X+2*N2O4X+NOX)/(N2X+O2X+NOX+NO2X+N2O4X)
C
C       SUMOUTNOX is an approximate percent of NOx in the offgas.
C
      IF ( SUMOUTNOX .GE. 2.5) THEN
C
C       This turns on the offgas feedback mechanism. The 2.5% level is a
C       guess at the point where emission problems occur.
C
                WATER=SUMOUTNOX
C
C       This is a guess at how to set the water flow level.
C
                IF (WATER.GT.4.) WATER=4.
C
C       4 gallons/minute represents the approximate maximum flow rate
C       currently attainable for water input to the column.
C
        ENDIF
C
 888   CONTINUE
      X= WATER * TIMESTEP
      A=0.
C
C       To start the liquid flow, the water to the top of the column in the
C       timestep is calculated and placed in the dummy variable X. The moles
C       HNO3 added, A, is set to zero.
C
      DO 700 I=44,1,-1
      HNO3(I)=HNO3(I)+A
      VOLUME(I)=VOLUME(I)+X
C
C       For each tray down to tray 1, the moles and volume transferred
C       from tray to tray is calculated and moved by adding the X and A
C       dummy variables to the tray variables.
C
C
        IF (VOLUME(I).GT.0.) THEN
           F=HNO3(I)/VOLUME(I)
        ELSE
                F=0.
        ENDIF
C
C       This recalculates the current acid concentration (does the mixing).
C
C
C       The next section calculates the volume transferred to the next tray.
C
      IF (VOLUME(I).LE.VOLMIN) THEN
        X=0.
C
C       If the tray volume is less than or equal to the absolute tray
C       minimum (here 23 gallons), no flow is allowed.
```

```
C
          GO TO 652
          ENDIF
        IF (VOLUME(I).LE.FULLVOL(I) ) THEN
          X= TRICKLEVOL
C
C         If the tray volume is less than the 'ideal' volume, only the
C         nominal draining of the column is allowed.
C
          GO TO 651
          ENDIF
        X= VOLUME(I) - FULLVOL(I) + TRICKLEVOL
C
C         If the tray volume is above the 'ideal' volume, the drain volume
C         and the excess are moved down.
C
651     IF ( X .GT. VOLUME(I) ) X = VOLUME(I)
C
C         Guarantees no negative tray volumes
C
        IF ( X .GT. .125 ) X = .125
C
C         This is an empirical maximum flow rate off each tray that was found
C         necessary to make the model results most closely match real data.
C
 652        IF (X .GT. 0.) THEN
          A=F*X
          HNO3(I)=HNO3(I)-A
          VOLUME(I)=VOLUME(I)-X
        ELSE
          A=0.
        ENDIF
C
C         If the transferred volume (X) is non-zero, the transferred moles
C         are calculated (or else set to zero) using the fraction F calculated
C         above. This volume and moles are subtracted from the current tray.
C         A and X are used either in the next DO loop pass or in the subsequent
C         code.
C
        IF (VOLUME(I).GT.0) THEN
             FHNO3(I)=HNO3(I)/VOLUME(I)
        ELSE
        FHNO3(I)=0.
        ENDIF
C
C         The IF recalculates the tray acid concentration.
C
 700    CONTINUE
        IF (X.GT.0.) THEN
C
C         If the volume off the last tray is non-zero, its effect on the acid
C         in the column bottom must be calculated.
C
          COLMOLES = COLMOLES + A
          COLVOLUME = COLVOLUME + X
          F = COLMOLES / COLVOLUME
C
C         The column.bottom moles (COLMOLES) and volume (COLVOLUME) is
C         incremented and a new acid concentration calculated.
```

```
C
          X = COLVOLUME - 180.
          COLVOLUME = COLVOLUME - X
          A= F*X
          COLMOLES = COLMOLES - A
C
C         This code assumes any volume above 180 gallons is immediately set
C         out to a tank. Thus that volume is calculated and subtracted from
C         the column bottom volume. The moles moved out are then calculated
C         and subtracted as well.
C
          VOL = X / TIMESTEP
          FXHNO3= F * .264172
C
C         For program output, the volume is converted to gallons/minute.
C         The acid concentration is converted to moles/liter here in
C         preparation for conversion to weight percent later.
C
        ELSE
          A=0.
          VOL = 0.
          FXHNO3 = 0.
C
C         No flow implies no product.
C
        ENDIF
        FXHNO3=.006025225*FXHNO3**3-.205523*FXHNO3**2+6.304383*FXHNO3
C
C         This converts HNO3 moles/liter to weight percent via a statistical
C         correlation used before.
C
        LOOPCOUNT=LOOPCOUNT+1
C
C         LOOPCOUNT is a flag used to tell the program when to print out
C         results. It is the number of program steps (timesteps) since
C         the last time it was zeroed.
C
        NOOUT = NOOUT + NOX/FCOUNT
        NO2OUT = NO2OUT + NO2X/FCOUNT
        N2O4OUT = N2O4OUT + N2O4X/FCOUNT
        N2OUT = N2OUT + N2X/FCOUNT
        O2OUT = O2OUT + O2X/FCOUNT
        HNO3OUT = HNO3OUT+ FXHNO3/FCOUNT
C
C         The 'OUT' subscript indicates the variables that hold the time
C         averaged offgas moles and acid concentrations. FCOUNT is the REAL
C         number of steps/minute.
C
        IF (LOOPCOUNT.EQ.MAXCOUNT) THEN
C
C         MAXCOUNT is the INTEGER number of steps/minute.
C
        MINUTE=MINUTE+1
C
C         MINUTE stores the number of minutes of elapsed time.
C
        REALHOUR = FLOAT(MINUTE)/60.
C
C         REALHOUR is the elapsed time in hours used in the output.
```

```
C
      WRITE(3, 99), HNO3OUT,NOOUT,NO2OUT,N2O4OUT,N2OUT,O2OUT,VOL,
     + DISNO2,DISNO,DENNO2,DENNO,REALHOUR,WATER
   99 FORMAT(1X, 6(F8.4,1X), F5.2, 4(1x,F8.4), 1X, F9.4, 1X, F8.4)
C
C       The calculation results are written to unit 3, a file defined
C       at the start of the program.
C
      LOOPCOUNT=0
      NOOUT=0.
      NO2OUT=0.
      N2O4OUT=0.
      N2OUT=0.
      O2OUT=0.
      HNO3OUT=0.
C
C       After a printout, the appropriate variables are zeroed.
C
      ENDIF
 2000   CONTINUE
  999 CONTINUE
      CLOSE(UNIT=3)
      CLOSE(UNIT=4)
C
C       FORTRAN file cleanup commands.
C
      ENDDO
C
C       The end of the MASTER loop.
C
      END
```

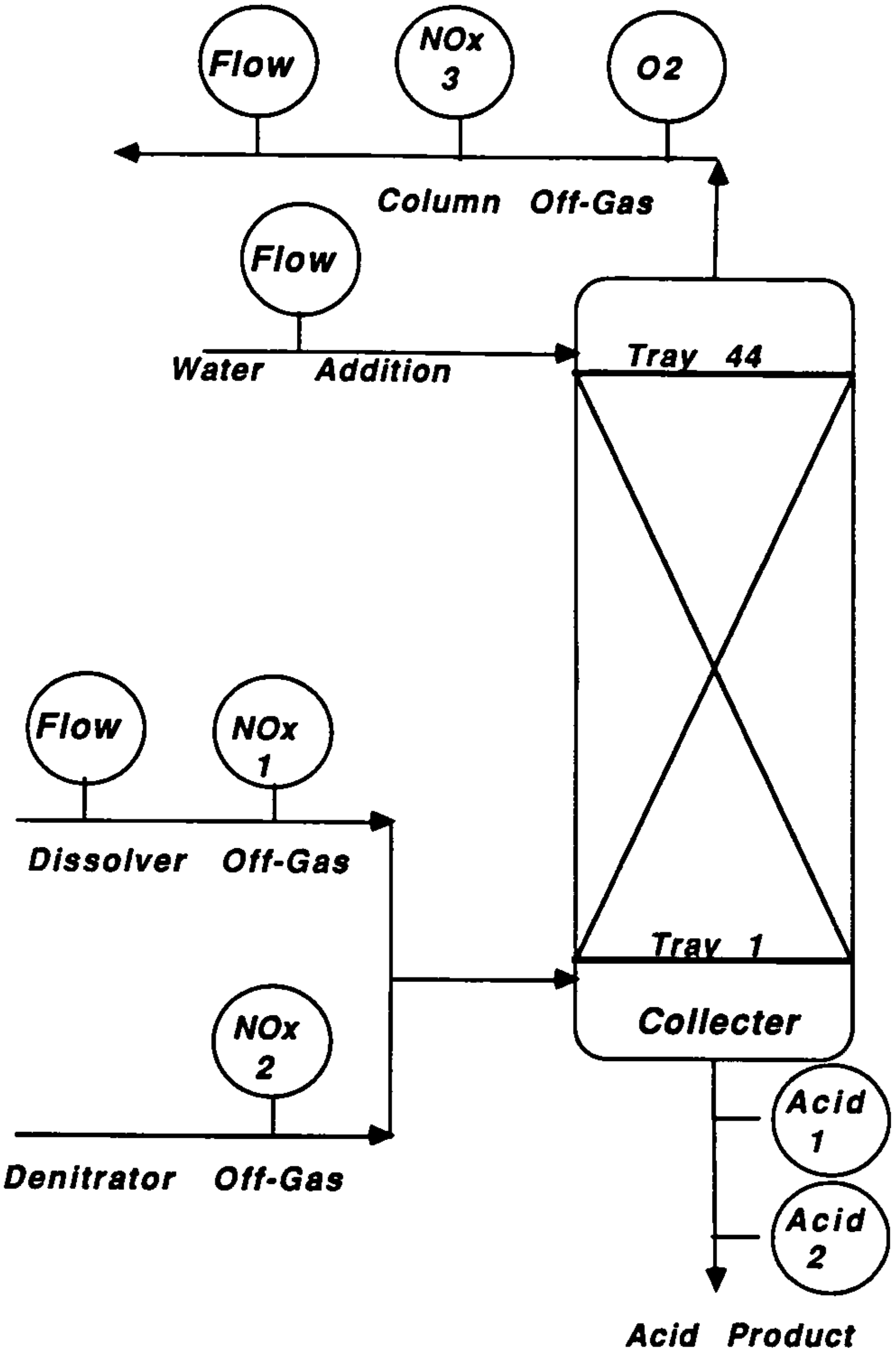


Figure 1. Skematic Diagram of the A-line Nitrogen Oxides Absorption Column showing gas and liquid streams and analysis points.

Figure 2. NO2 Composition Profiles from July 10, 1988 Dissolver Run

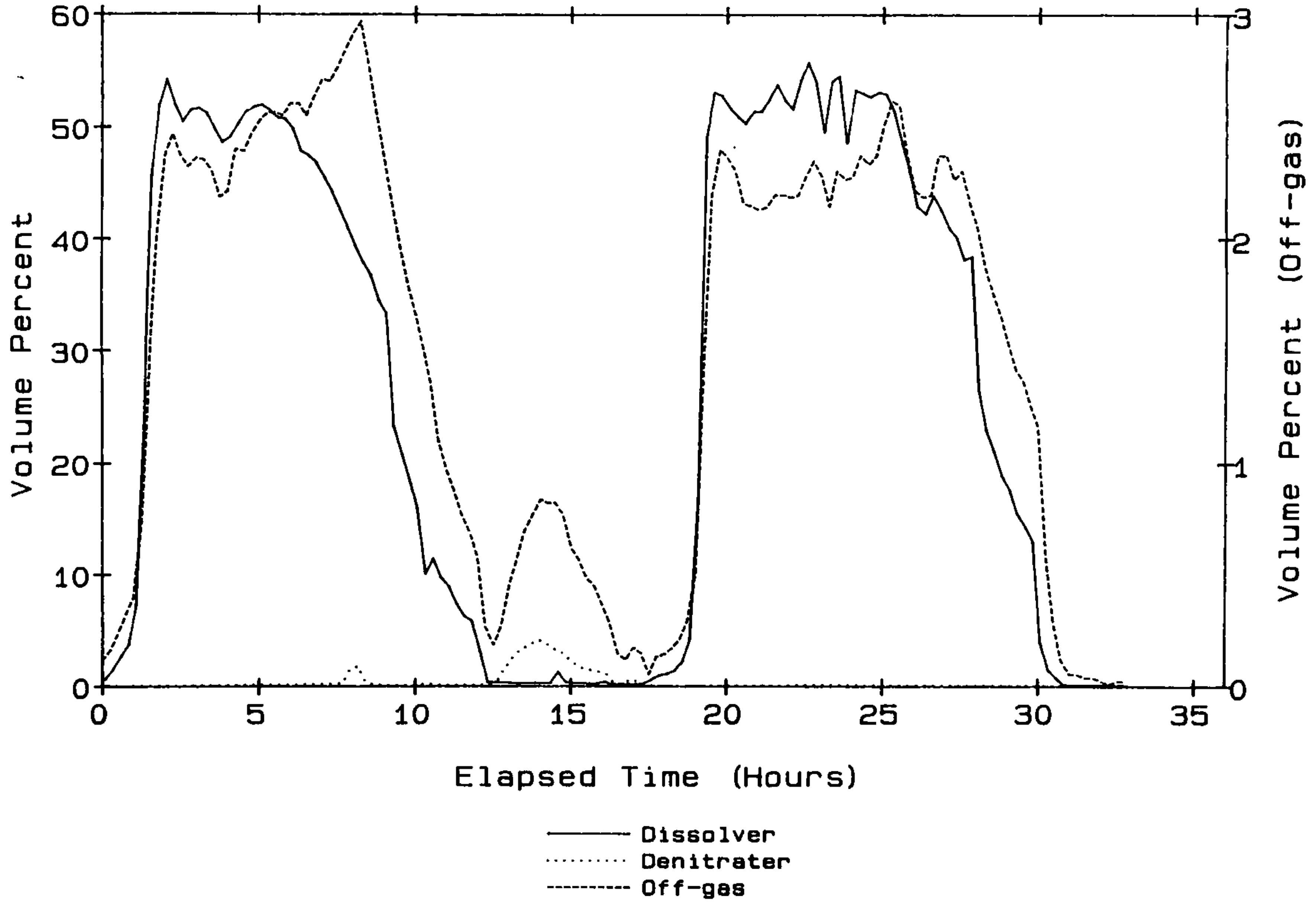


Figure 3. NO Composition Profiles from July 10, 1988 Dissolver Run

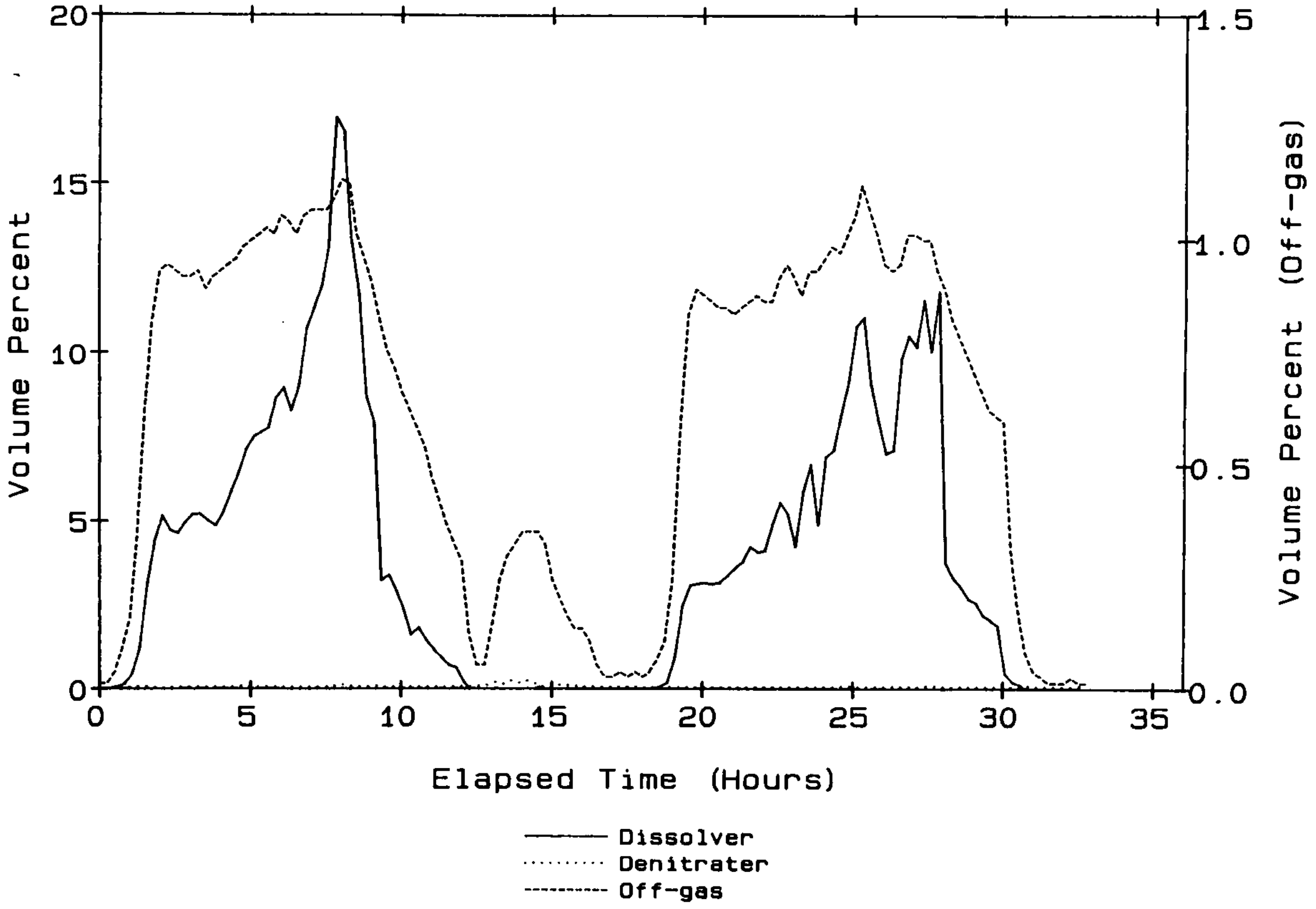


Figure 4. Gas Flow Rates from July 10, 1988 Dissolver Run

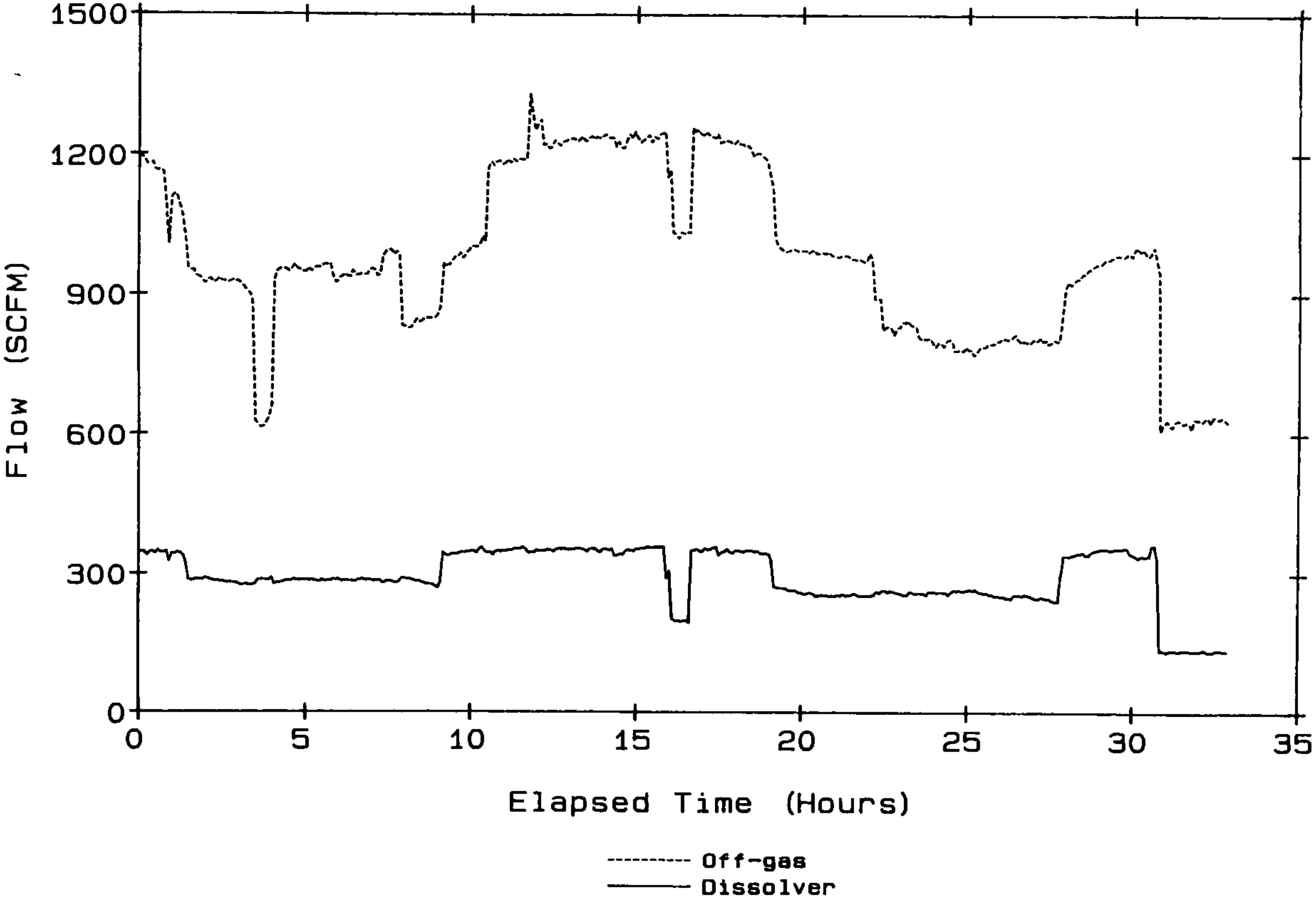


Figure 5. Nitric Acid Composition Profiles from July 10, 1988 Dissolver Run

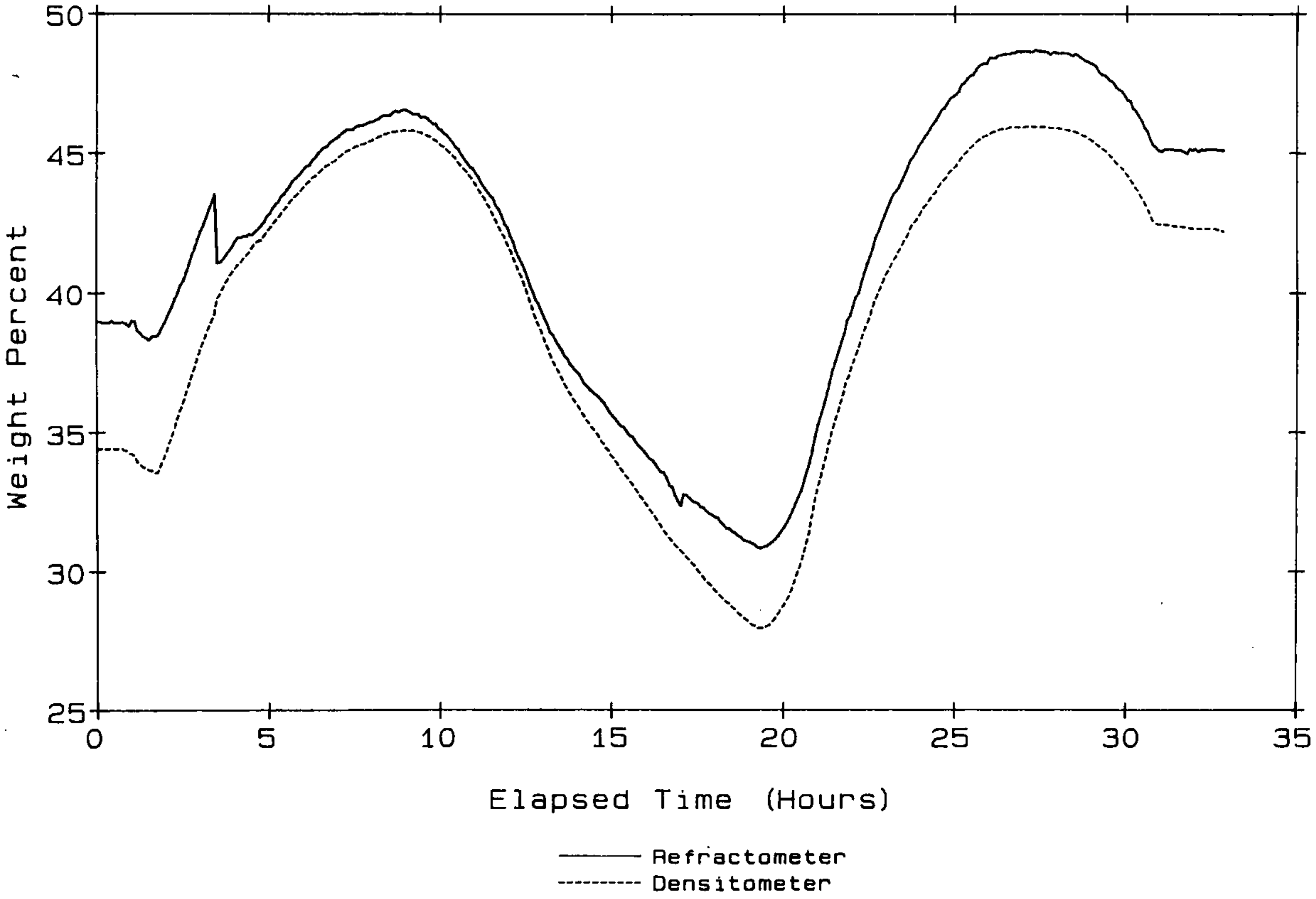


Figure 6. Feed Water Flow and Off-gas Oxygen Composition Profiles for July 10, 1988 Dissolver Run

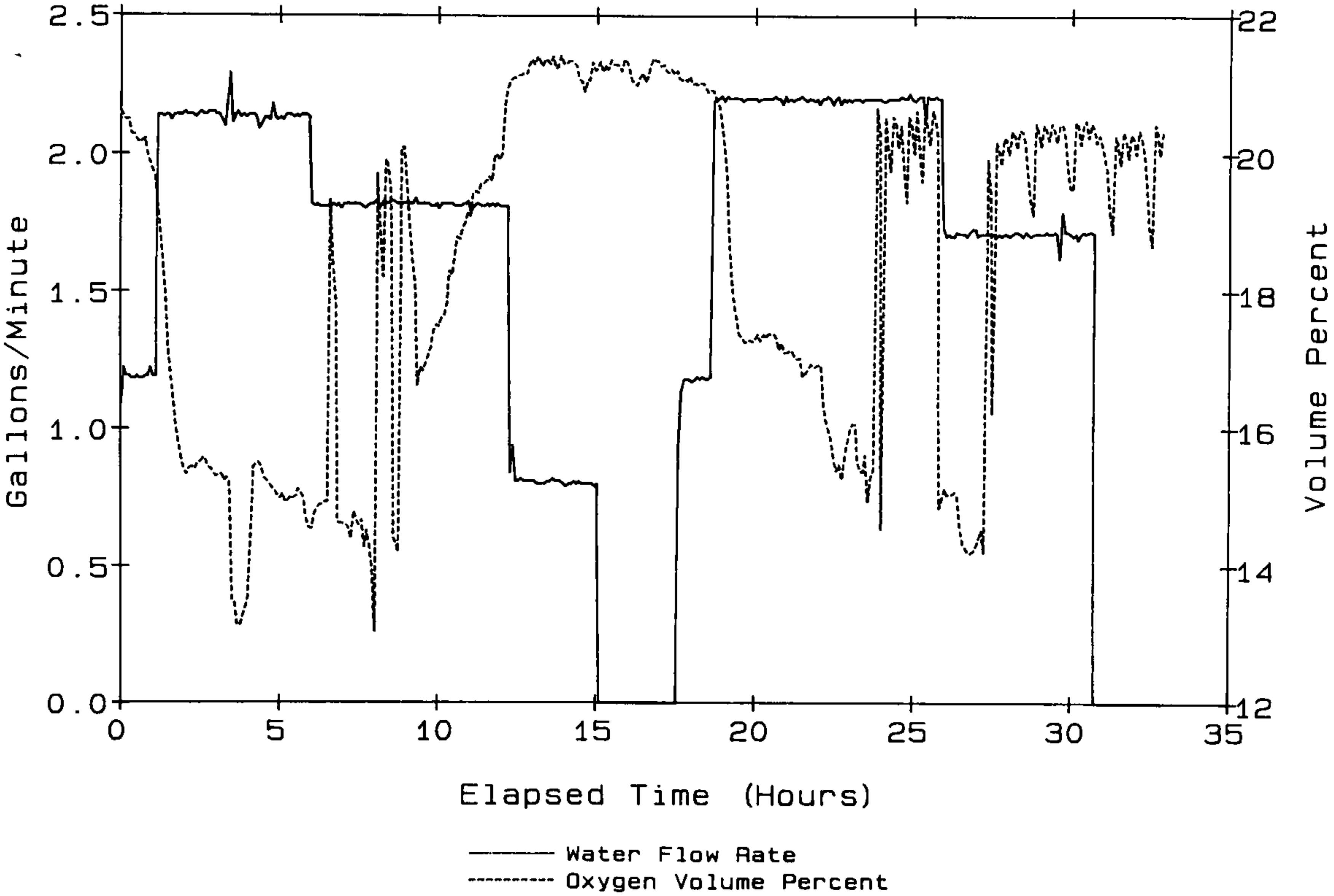


Figure 7. NO2 Composition Profiles from July 25, 1988 Dissolver Run

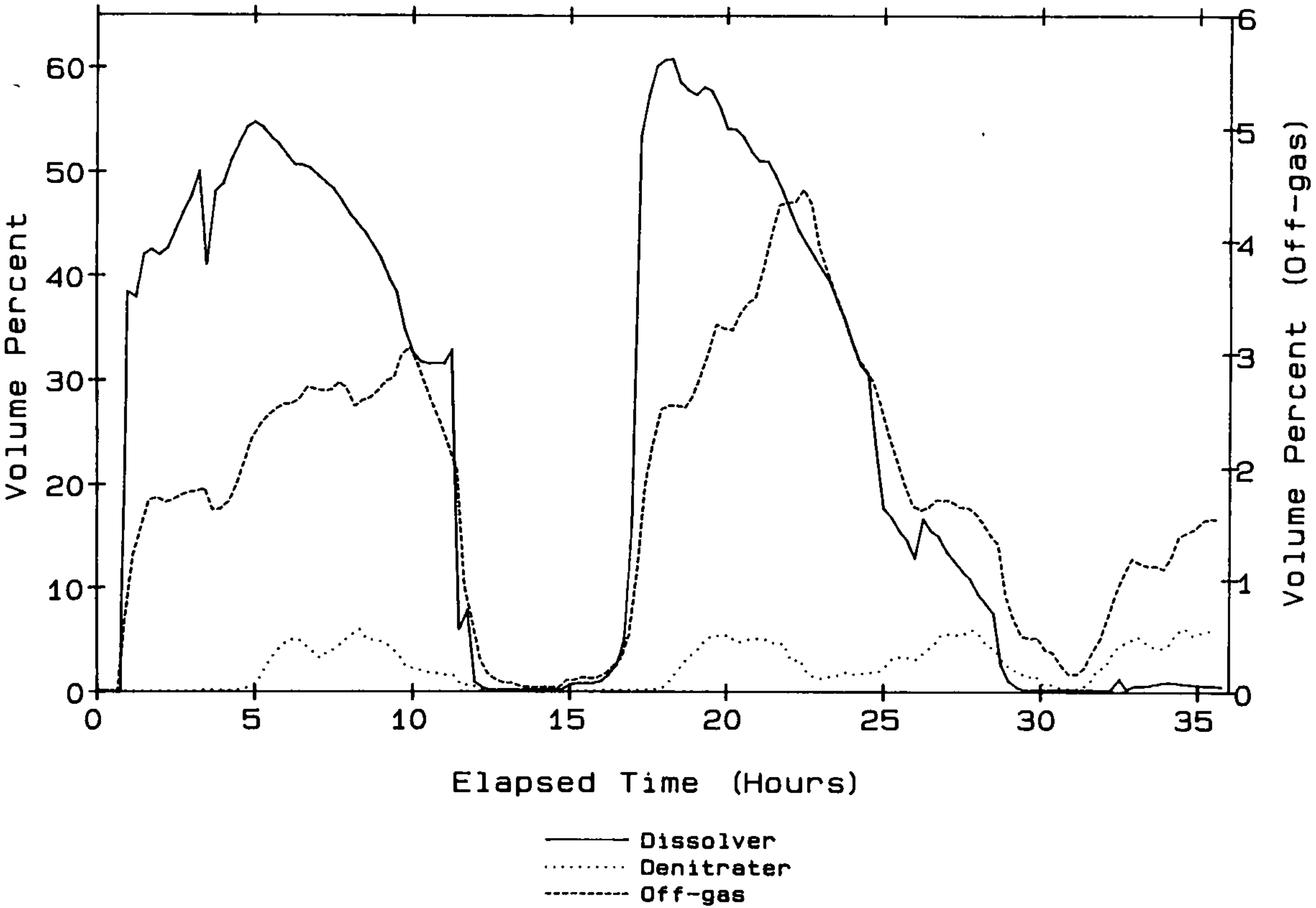


Figure 8. NO Composition Profiles from July 25, 1988 Dissolver Run

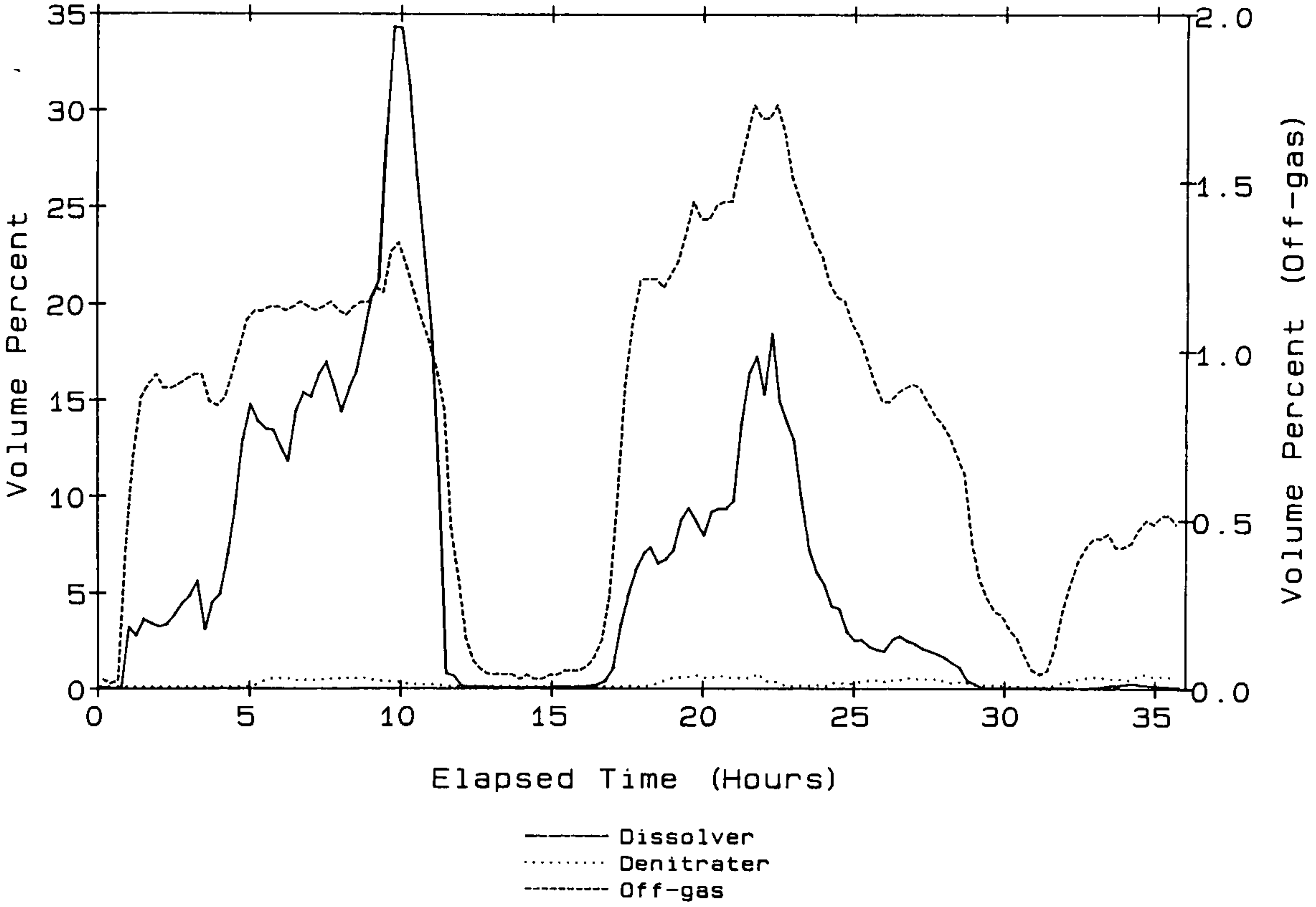


Figure 9. Gas Flow Rates from July 25, 1988 Dissolver Run

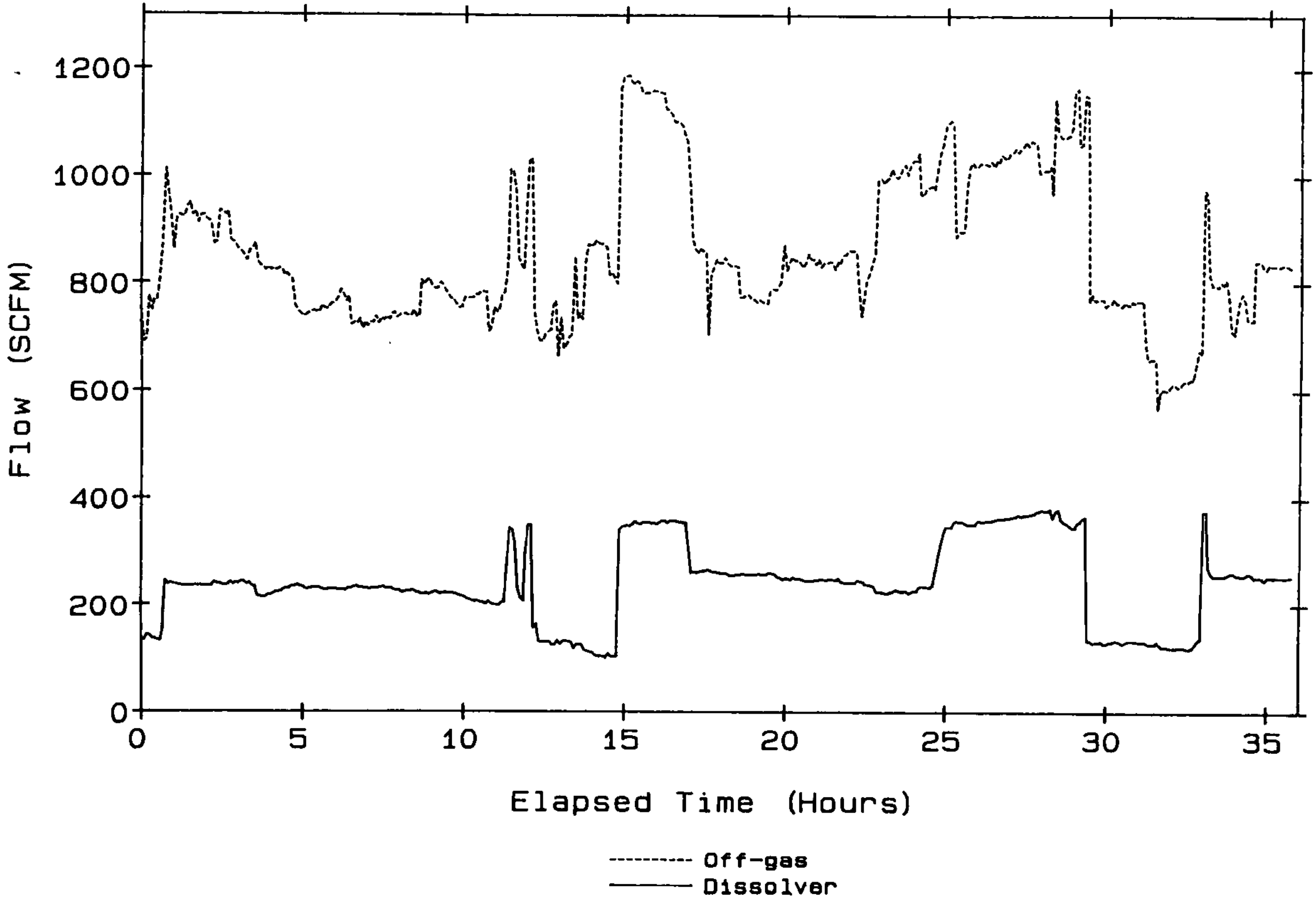


Figure 10. Nitric Acid Composition Profiles from July 25, 1988 Dissolver Run

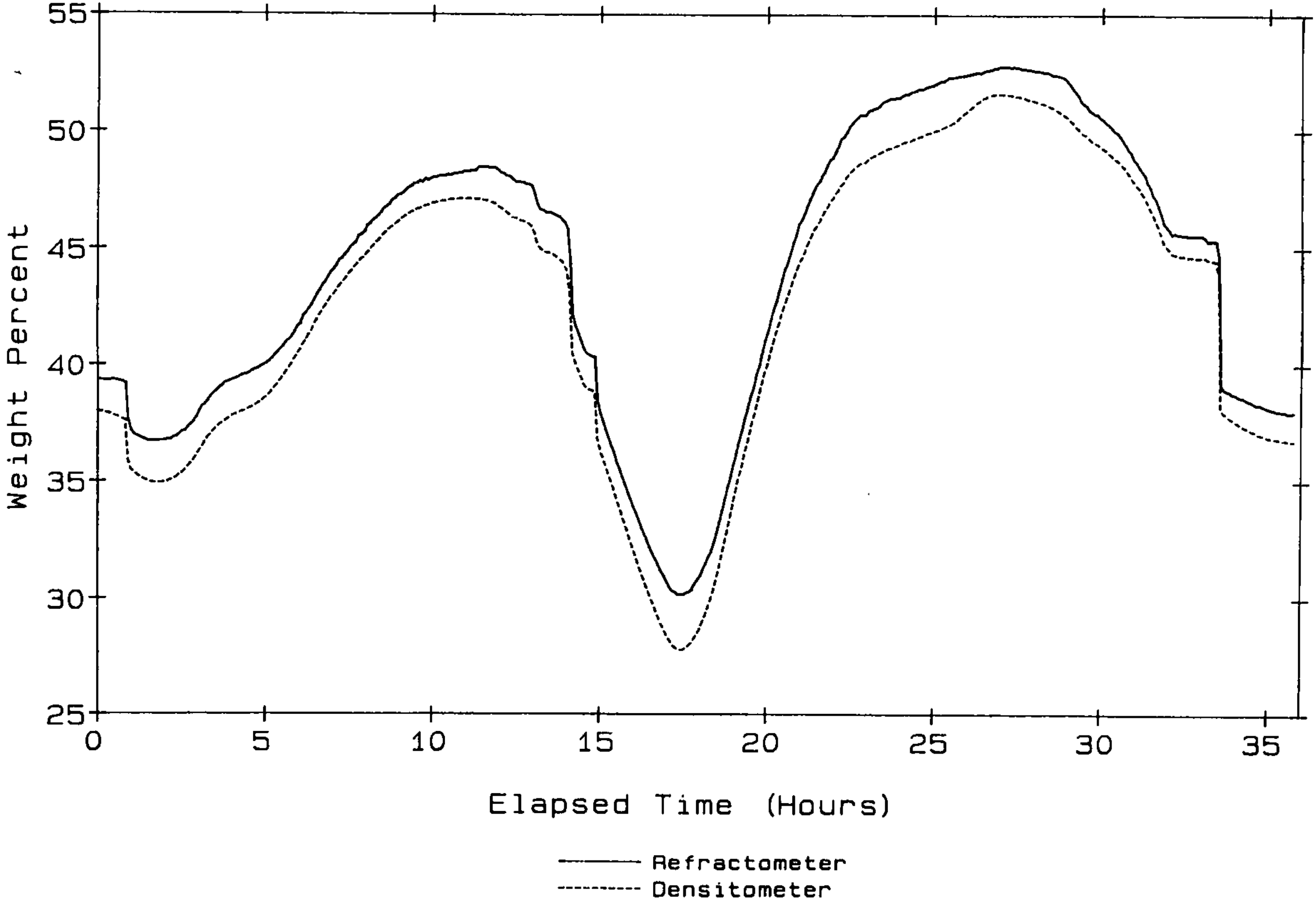


Figure 11. Feed Water Flow Profile for July 25, 1988 Dissolver Run

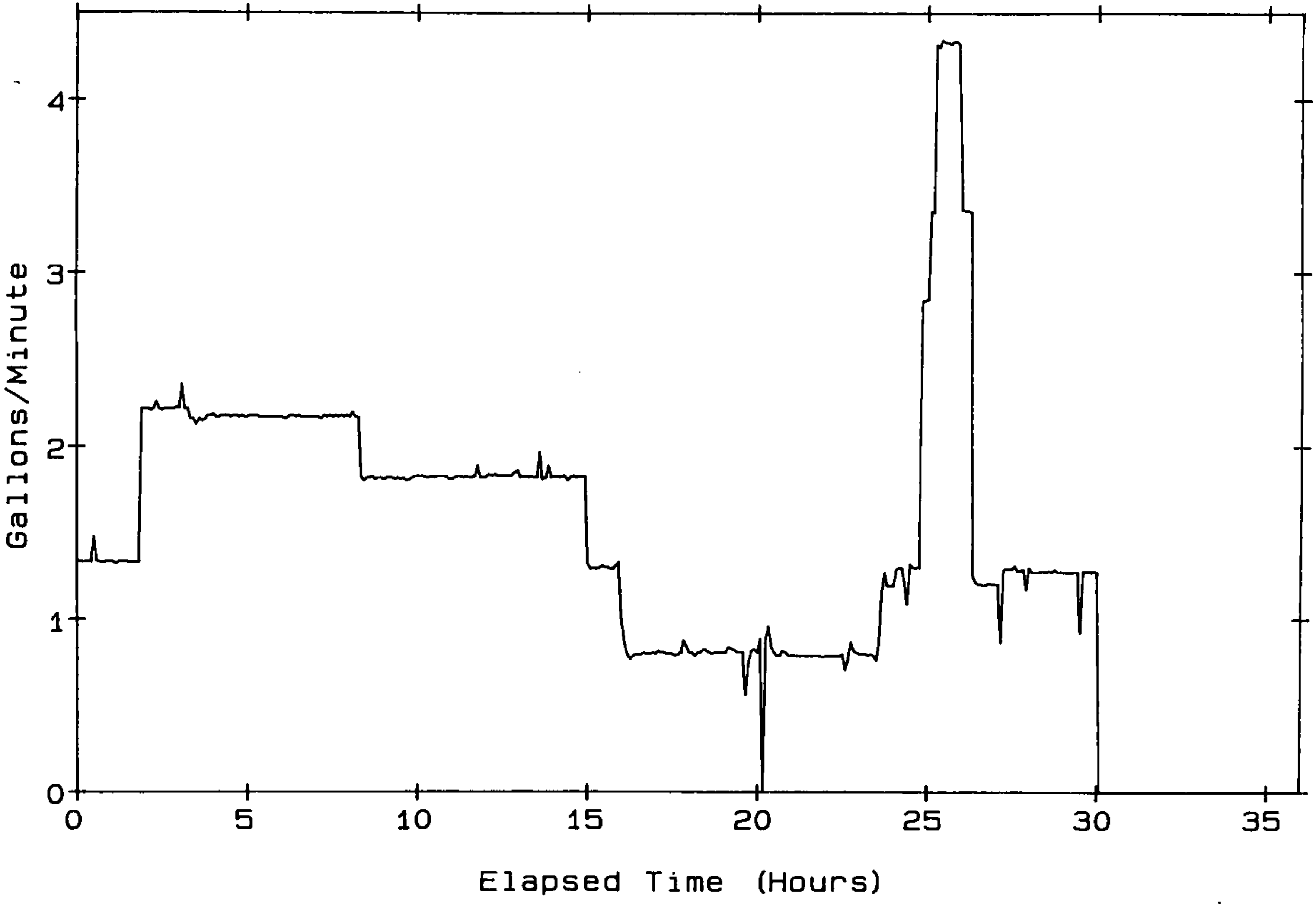


Figure 12. Comparison of Actual and Calculated NO2 Composition Profiles from July 10, 1988 Dissolver Run

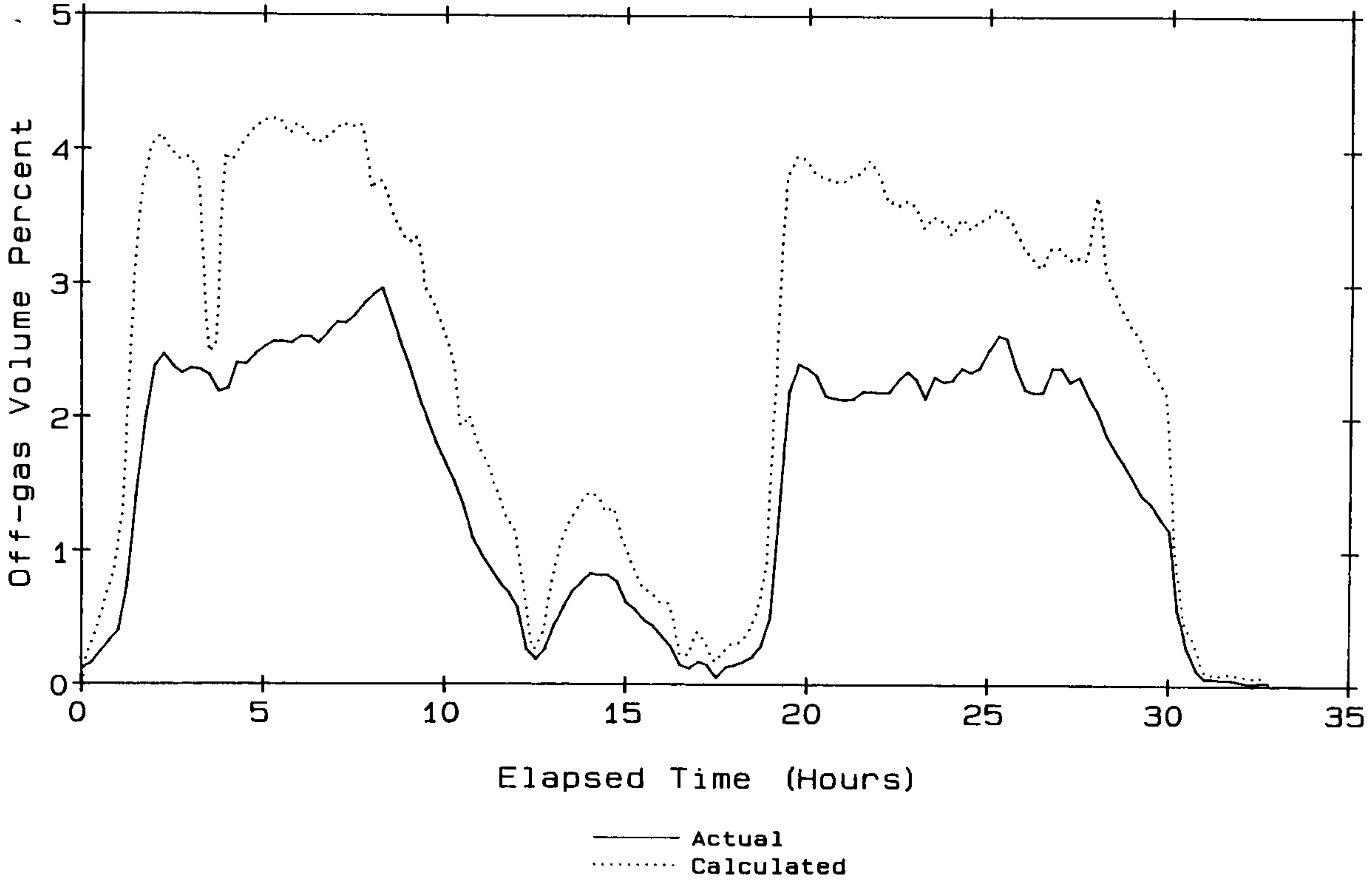


Figure 13. Comparison of Actual and Calculated NO Composition Profiles from July 10, 1988 Dissolver Run

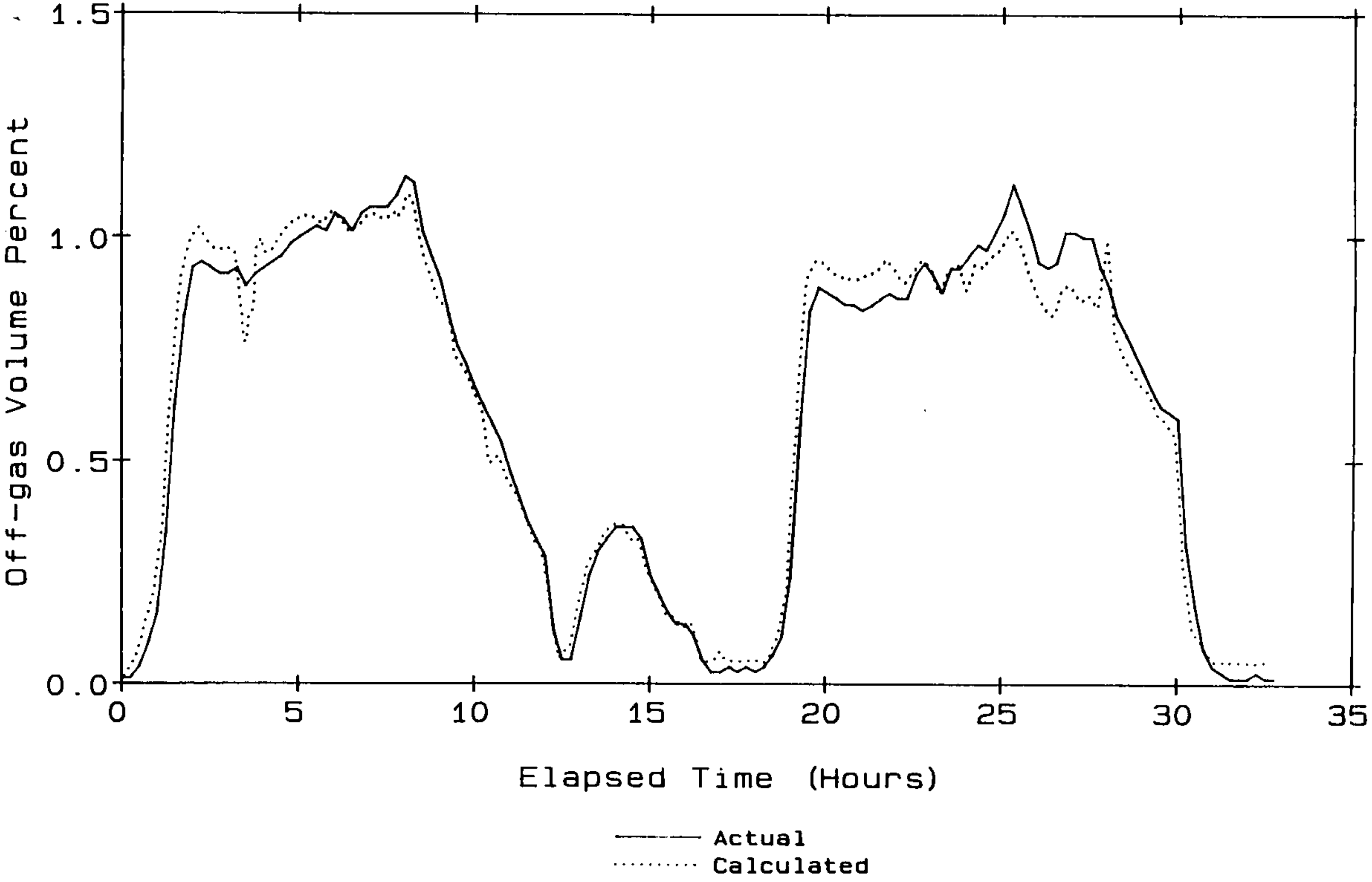


Figure 14. Comparison of Actual and Calculated Nitric Acid Composition Profiles from July 10, 1988 Dissolver Run

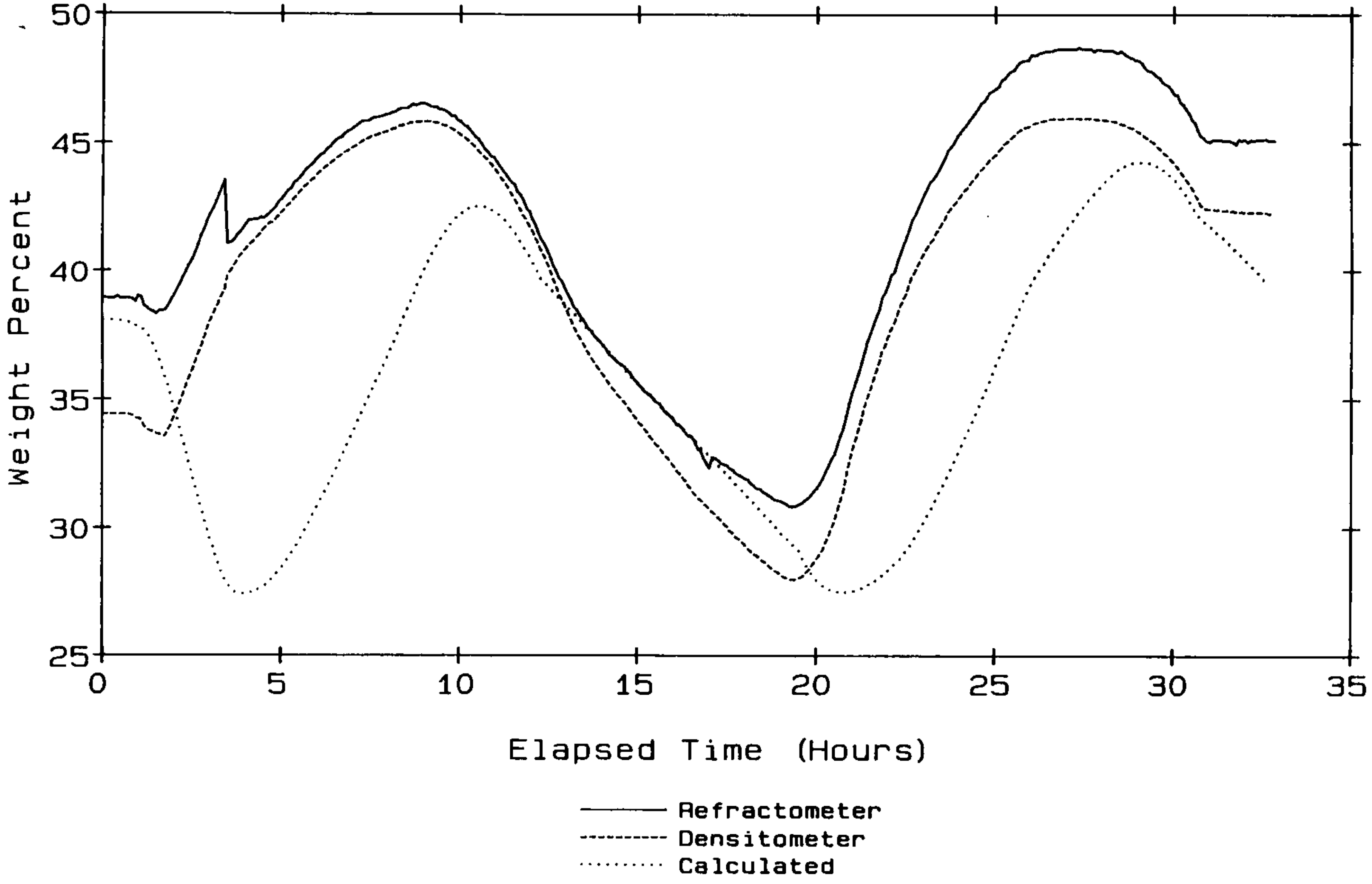


Figure 15. Comparison of Actual and Calculated NO2 Composition Profiles from July 25, 1988 Dissolver Run

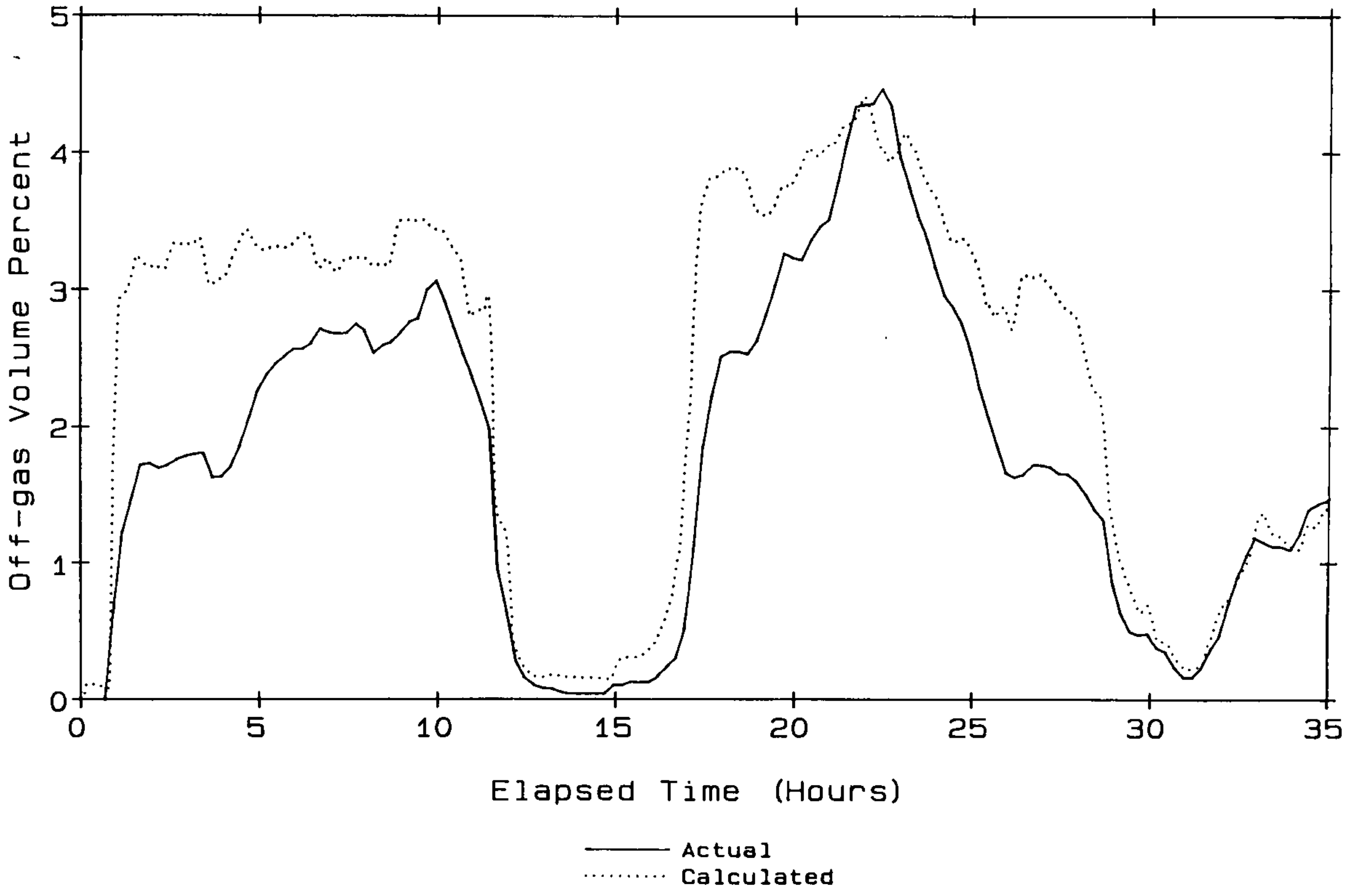


Figure 16. Comparison of Actual and Calculated NO Composition Profiles from July 25, 1988 Dissolver Run

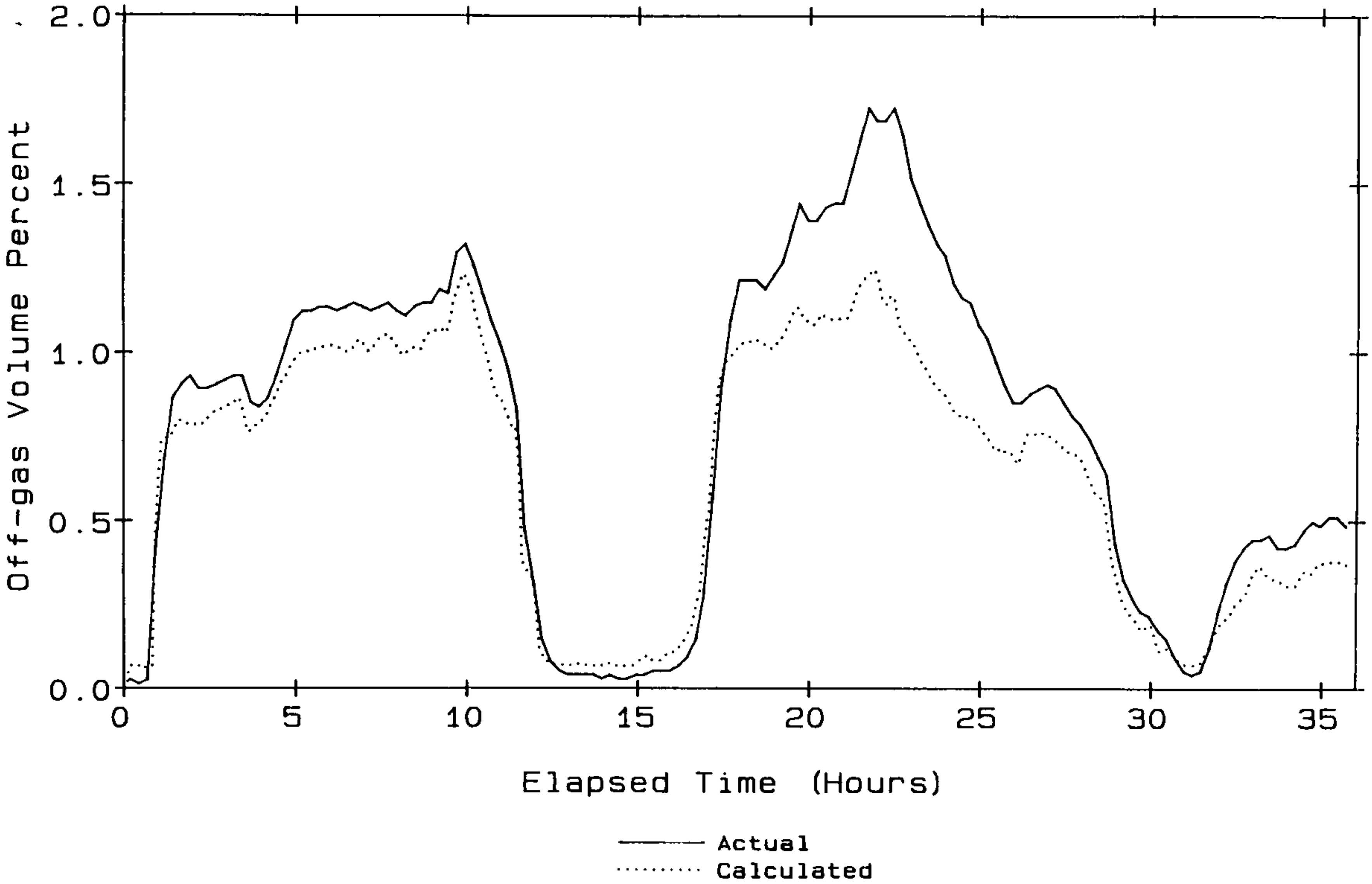


Figure 17. Comparison of Actual and Calculated Nitric Acid Composition Profiles from July 25, 1988 Dissolver Run

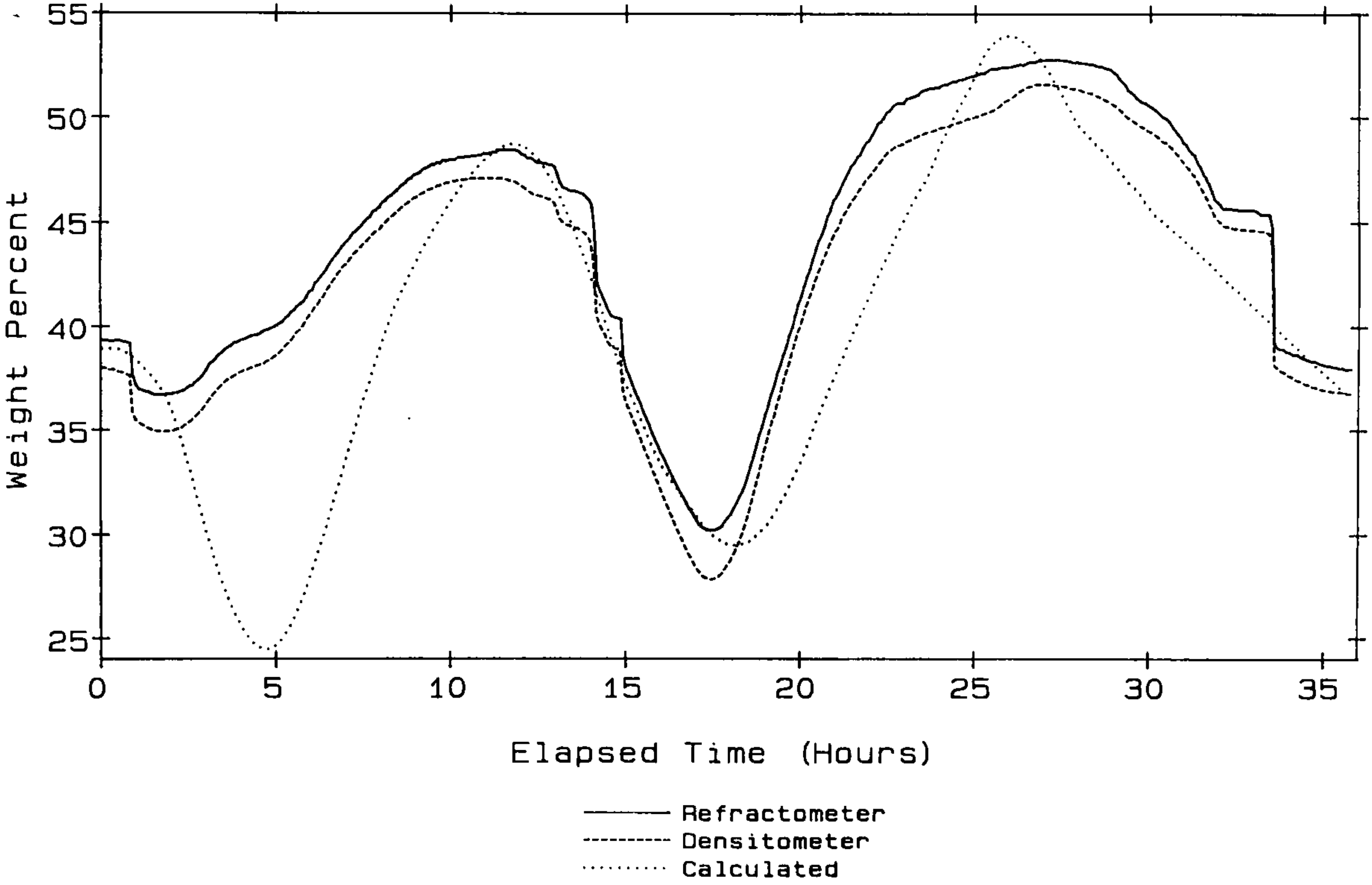
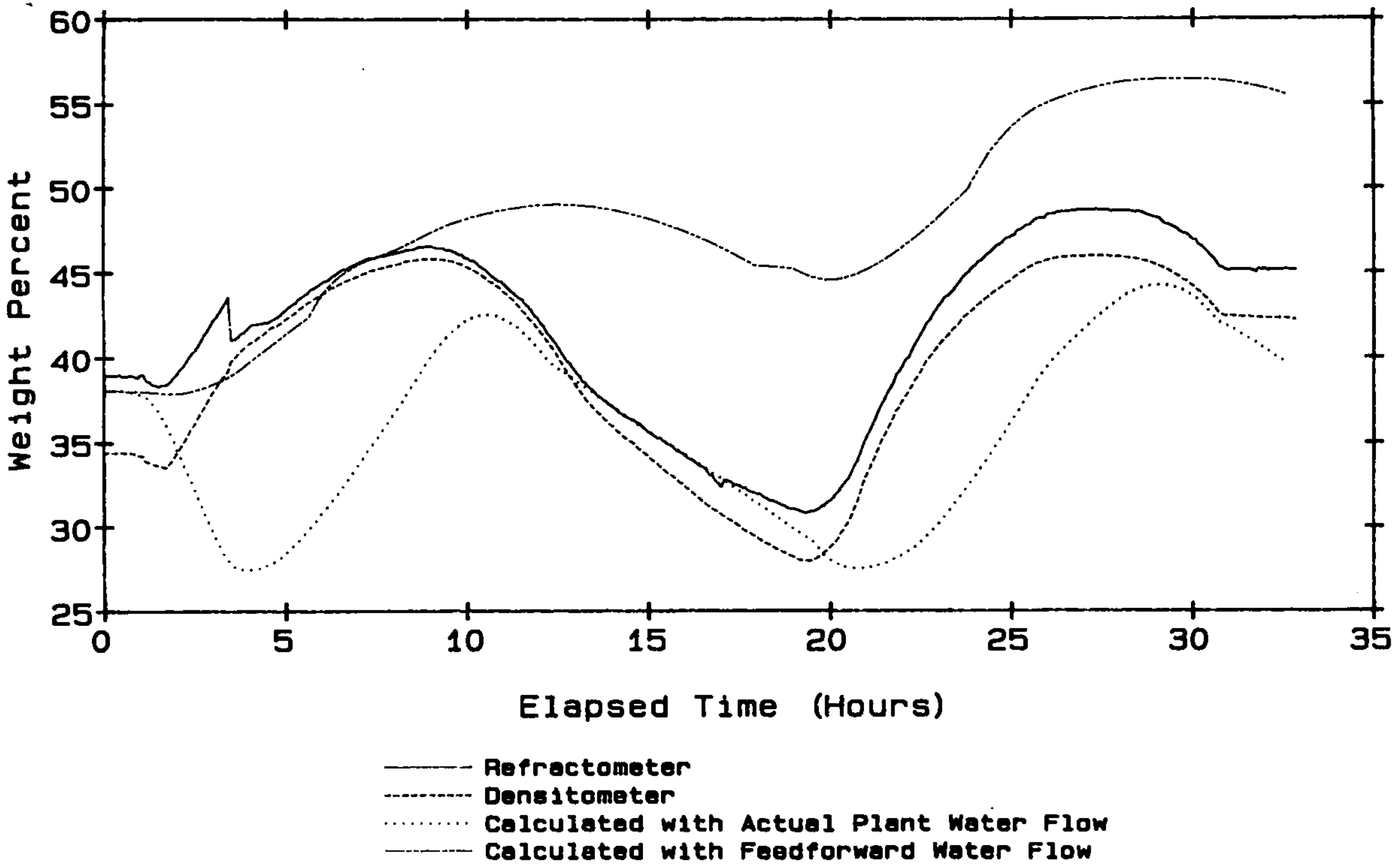


Figure 18. Comparison of Actual and Calculated Nitric Acid Composition Profiles from July 10, 1988 Dissolver Run (Using Actual Plant Water Flow and NOx Feed-Driven Feedforward Water Flow)



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AUTHOR(S) K.L. Shanahan, S.F. Peterson   PHONE NO. 5-5257; 5-5251

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