AN APPARATUS FOR THE STUDY OF VOLATILIZATION REACTIONS

AN APPARATUS FOR THE STUDY
OF THE VOLATILIZATION OF
IRON SPECIES WITH
PENTANEDIKETONE LIGANDS

By

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ABSTRACT

An apparatus was designed and built to enable the study of volatilization reactions using a novel variant of thermogravimetry called thermoradiometry. The usefulness of the apparatus was demonstrated by investigating the volatilization of iron from solid samples with the fluorinated ligands 1,1,1-trifluoro-2,4-pentanedione and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione.

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1. INTRODUCTION

1.1 Volatilization

During studies on the impact of metal compounds on the environment, it is desirable to not only determine the concentration of an element but also the chemical form or species of the metal. For liquid or gaseous samples, a number of methods for the speciation of metals are known, such as chromatography, polarography, and selective adsorption onto various substrates. For solid samples, however, speciation is much more difficult as the chemical state of the analyte will change in the process of producing a solution or otherwise handling the analyte.

A potential method for the speciation of solid samples may be the selective volatilization of different chemical species out of the sample matrix followed by collection and subsequent analysis of the fractions. If a reactive gas is used as a volatilizing agent, if new species are formed from the elements of interest, and if it is assumed that the original compounds will react in different ways and at different temperatures, then the release of an element during volatilization will, at least partially reflect the original forms in which the element was present. This process may provide an indirect method for the speciation of trace elements in solid samples [1].

Volatilization of the analyte out of the sample matrix is a useful method of preconcentration [2]. Also the reactive gases used to produce the volatile species are usually easy to purify with respect to the analyte, and add very little contamination of the sample. Once the volatile form of the analyte is formed, it can be detected on-stream, or it can be collected and subsequently detected off-stream by a variety of analytical techniques.

The volatilization of metallic species, however, usually involves the use of corrosive or toxic gases, for example CO, HF, Cl_2, or CCl_4. High reaction temperatures, in the range of 600-1000 °C, are often necessary; thus, limiting the general applicability of the method. Volatile metal species such as hydrides, halides and alkyls are also often sensitive to atmospheric water or oxygen and great care must be taken to protect these species [1].

1.2 β-Diketone Ligands

The diketone ligand, 2,4-pentanedione (acetylacetone), and its fluorinated derivatives have been used extensively by analytical chemists to produce stable and volatile metal chelates. These bidentate ligands generally produce neutral complexes with metal ions that have a coordination number twice the electronic charge of the metal ion. Figure 1 indicates which elements produce volatile complexes with ligands. Once produced these volatile chelates have a number of uses, most notably the separation and determination of metals by gas chromatography of the chelates. As these chelates are uncharged and lipophilic in nature, they are also used for the extraction of metals from aqueous solution into an organic phase.

The fluorinated β-diketone ligands 1,1,1-trifluoro-2,4-pentanedione H(tfa) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfa) are often employed for the production of volatile chelates due to their high volatility, thermal stability and reactivity, properties which increase with increasing fluorination (see Table 1). The high electronegativity of the perfluoromethyl group increases the acidity of the ligand by more than two orders of magnitude as one moves from acetylacetone to H(tfa) and by an other two orders of magnitude as one moves from H(tfa) to H(hfa) [3]. Ligand volatility increases with additional fluorination due to increased intramolecular hydrogen bonding, and formation of a repulsive fluorocarbon shell structure [4]. The volatility of the metal chelates formed by these ligands also increases with increasing fluorination, due to the formation of a repulsive fluorocarbon shell around the central metal ion.

The ability of these fluorinated ligands to chelate metals has been put to use in the extraction of metals from

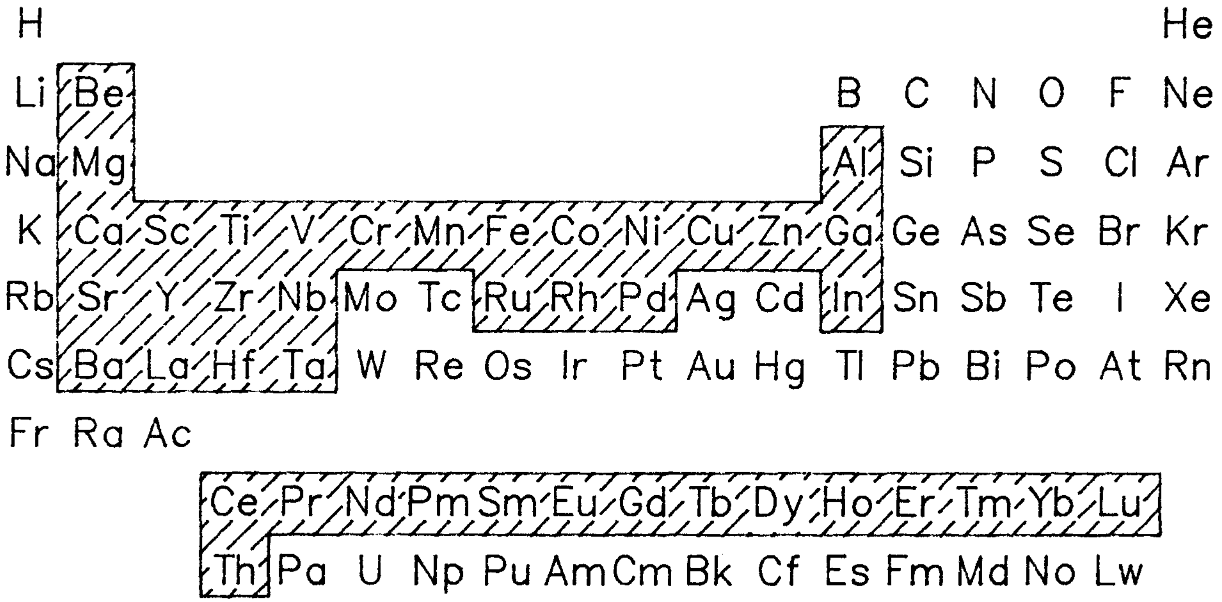


Figure 1 Elements forming volatile chelates with β-diketone ligands

Table 1: Properties of β-diketone Ligands [3]

β-diketone ligand	pKa*	boiling point (760 mm)
2,4-pentanedione	8.9	140 °C
1,1,1-trifluoro-2,4-pentanedione	6.7	107 °C
1,1,1,5,5,5-hexafluoro-2,4-pentanedione	4.6**	70 °C

* in distilled water, 23 °C

** determined as the dihydrate in water

ore and alloy samples [5]. Samples are usually placed in a sealed quartz tube with the ligand and heated. When extracting metals from alloys the ligands act as oxidizing agents, producing hydrogen gas as they oxidize and chelate the metal. While there is extensive use of these ligands in the liquid phase for extracting metals from solid samples, there is no indication in the literature that they have been used in the gas phase for the production of metal chelates from solid metal samples.

These ligands would be useful as volatilization reagents for several reasons. Their reactivity and the volatility of the resulting chelates should enable the use of relatively low temperatures for extraction and transport of metals. The ligands have a low order of toxicity, are readily available, and are easily purified of metal containing impurities. The diketone ligands are selective in that they preferentially chelate hard transition metal species such as iron, manganese, chromium and the lanthanides. Selectivity for different metal species may be provided by temperature and/or ligand programming during an extraction.

1.3 Thermal Analysis

Volatilization reactions carried out at a constantly increasing temperature are analogous to thermogravimetric analysis, which should allow thermogravimetric models to be used for the processing of volatilization data.

Most kinetic analysis methods for thermogravimetric data involve the use of the Arrhenius equation modified for non-isothermal conditions [6]. The rate of volatilization can be defined as $d\alpha/dt$, where α is the normalized fraction of the initial sample reacted. The fraction of sample remaining is thus $(1-\alpha)$. In an isothermal process, the volatilization rate will depend only on the fraction of sample remaining;

$$(d\alpha/dt) = k\ f(\alpha). \tag{1}$$

In a nonisothermal process such as thermogravimetry, the rate constant k will vary with temperature. The Arrhenius equation describes the dependence of the rate constant on temperature;

$$k = A \exp(-E_a/RT), \tag{2}$$

where A is the frequency factor, E_a is the activation energy, and R is the gas constant.

As thermogravimetry uses a constant heating rate the substitution

$$q = dT/dt \tag{3}$$

can be made. Equations 1, 2, and 3 can be combined to eliminate the rate constant k;

$$(d\alpha/f(\alpha)) = (A/q) \exp(-E_a/RT)\ dT\ . \tag{4}$$

This equation is used in the differential method of thermogravimetric analysis [7] after rearranging, to give an expression of the form

$$\ln[(1/f(\alpha)) * (d\alpha/dT)] = \ln (A/q) - E_a/RT . \quad (5)$$

When the left hand side of equation 5 is plotted against 1/T, a straight line is obtained from which E_a and A can be obtained.

The expression ($d\alpha/dT$) in equation (5) is best obtained by numerically differentiating the thermogravimetric data by the method of cubic splines [8].

The form of $f(\alpha)$ depends upon the nature of the reaction. In the case where all the products are in the gas phase, such as volatilization reactions, this function is usually given as

$$f(\alpha) = (1-\alpha)^n \quad (6)$$

with the value of n being unity [9].

This type of analysis assumes that only one reaction is dominant over the temperature range of interest. The relative contributions of various competing reactions will vary with temperature, and therefore simple kinetic analysis should be done over a small temperature range.

1.4 Aim and Approach of Research

The aim of this research was to determine the feasibility of trace metal volatilization using β-diketones as a method of preconcentration and speciation for the analysis of air particulate samples. As such the project entailed the design, construction and commissioning of equipment suitable for volatilization of trace metals; the development of a method for monitoring trace metal volatilization reactions; collection of data on the volatilization of several species of a selected element; and the conversion of the raw data into useful information.

The method developed for the study of the reactions between the gaseous ligands and the solid samples was a novel method of thermal analysis. The use of radioactive samples allowed the activity of the reactant to be monitored as a function of time. The analyte was reacted with a gaseous ligand that produced a gaseous product which was swept away from the reaction site. The resulting change (decrease) in sample activity, as a function of temperature was used as a pseudo thermogravimetric trace. As the radioactivity of the sample was monitored as a function of temperature rather than sample weight, the technique could be called thermoradiometry.

Iron was selected as the main element of study for a number of reasons. Iron has a favorable radiochemistry; the main activated isotope is ^{59}Fe formed by the ^{58}Fe(n,γ)^{59}Fe reaction which has a thermal neutron cross-section of 1.23 barns, although the target has a natural abundance of only 0.33 %. The product isotope has a half-life of 45 days, so sample decay during a volatilization will be negligible. The product isotope emits predominately two gamma rays at 1291 and 1099 KeV, with absolute intensities of 44% and 56%, respectively, making detection of the radioactive species simple. Iron also exhibits a number of stable oxidation states and a variety of species, including such species as mixed oxides. This would make the study of iron interesting from a speciation point of view.

2. EXPERIMENTAL PROCEDURES

2.1 Design of volatilization apparatus

The apparatus for obtaining thermoradiometric data was designed to satisfy a number of design specifications and concepts.

The primary constraint on the design was the isolation of the radioactive sample and chelates from the general environment. As the chelates are lipid soluble it was necessary that the metal ions be immobilized as soon as possible after they were transported from the sampling site and were no longer needed in a volatile form.

Another major design consideration was a system for the delivery of the ligand as a vapour to the sample site and its recovery for reuse. As the ligands tend to slowly form solid dihydrates, the ligand cycle had to be designed as a closed, dry system.

As the proposed method being developed demanded that the sample temperature increase at a known reproducible rate, a mechanism for heating the sample had to be designed and incorporated into the apparatus. The temperature ramp generated by the heating mechanism should be linear over the temperature range of 125 to 450 °C, and thus the sample area should be stable at temperatures up to 500 °C.

The design of the apparatus also had to include a method of monitoring the actual sample temperature as the sample and apparatus are being heated. If the sample were to be even slightly insulated from the heat source, the sample temperature might lag behind the set temperature ramp by several degrees Celsius. The method developed for monitoring the temperature of the sample also had to present the temperature data in a form that is useful and easy to manipulate.

The apparatus design also had to incorporate a method for monitoring the extent of reaction as a function of time. As the detection of radioactivity was to be used for determining the amount of sample remaining, the apparatus design had to employ a suitable detector and geometry to give high counting efficiency, yet keep the background counts, from both the environment and transported sample, to a minimum. The design also had to ensure that the detector electronics were shielded from the electromagnetic noise associated with the heating elements and motors used in other subsystems of the apparatus.

The design of the data collection systems had to allow for later manipulation of both data sets off-line. The data acquired thus had to be in a computer readable form. The two data sets also had to be collected in such a manner that they could be correlated during processing.

The apparatus was also designed to be modular in nature. A modular design allowed parts of the apparatus to be modified or replaced without extensive alteration to the apparatus as a whole.

2.2 Construction of volatilization apparatus

The apparatus was constructed in our laboratory following the above design specifications. A schematic diagram of the apparatus is given in Figure 2. The apparatus as a whole was constructed of a number of subassemblies, described below.

Extraction Tube

The extraction tube was constructed of glass with teflon-lined sliding screw connections (Sovirel SVL). Surfaces exposed to hot ligand vapour were thus either glass or Teflon. It was comprised of a cylinder, (30 cm x 2.7 cm I.D.), wrapped with an armored wire heating element. The element was powered by a programmable temperature controller (Omega CN 2010),capable of generating eight sequential temperature/time profiles, each up to 90 minutes in length. A thermocouple lead to the controller was located between the extraction tube and the heating coil so that a linear temperature ramp could be maintained by the controller. The whole was then well wrapped with asbestos insulating tape.

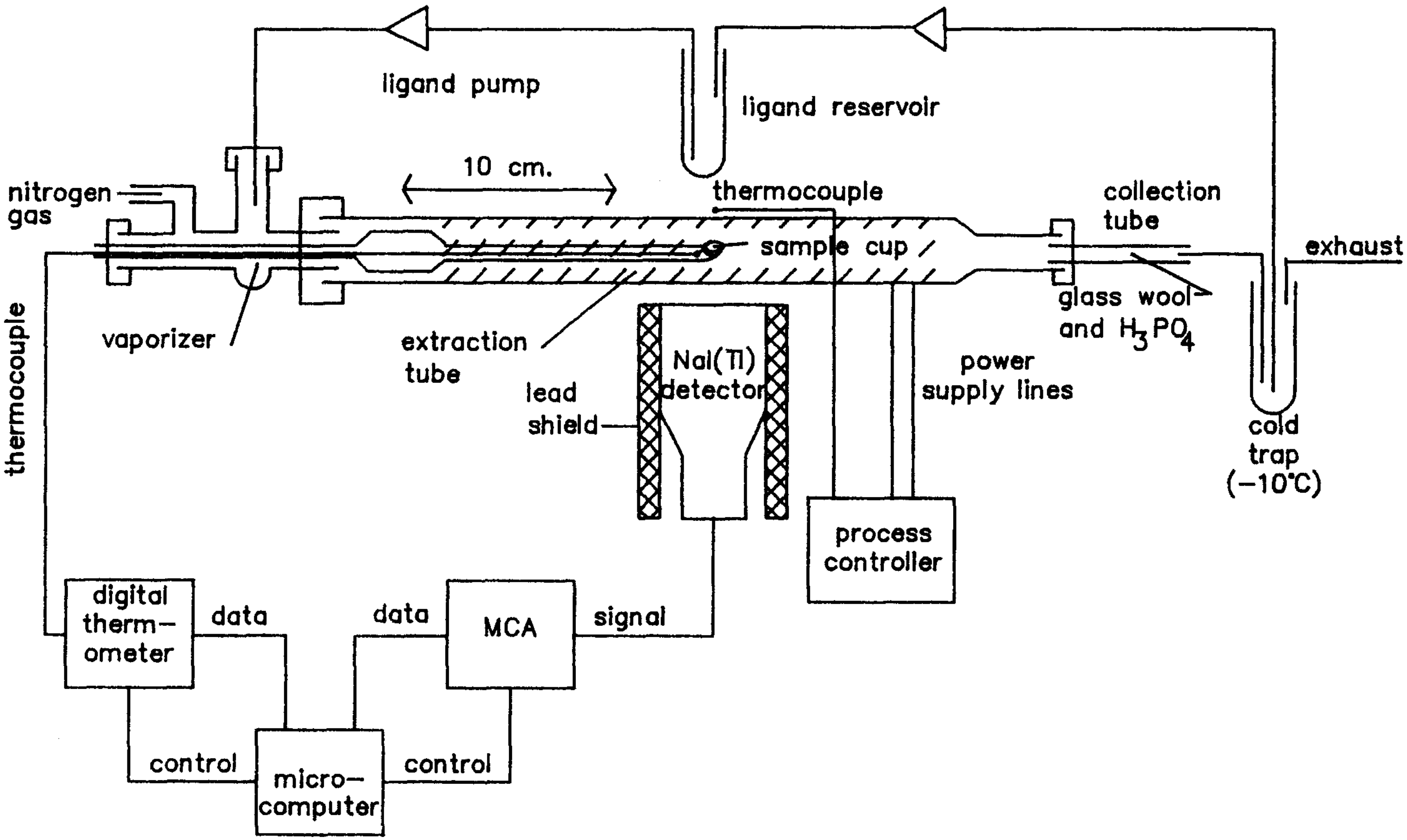


Figure 2 Volatilization Apparatus

This allowed extraction temperatures in the range from 100 °C to 500 °C to be used.

Ligand Delivery System

Ligands used in the extraction where stored in a glass reservoir with a teflon-lined stopper. The ligand was delivered to the vapourizer via reusable high density polyethylene tubing at a rate of 15 mL hour^{-1} using a peristaltic pump. The vapourizer was heated with heating tape powered by a Variac power supply and was maintained at a nominal temperature of 160 °C . The ligand vapour was carried in a stream of dried nitrogen gas (40 mL min^{-1}) over the metal sample and through the collector. It was then condensed in the cold trap and recycled.

Sample Holder

The sample holder was a hollow glass rod 30 centimeters long and eight millimeters inside diameter. It was closed at one end, and held in place with a sliding screw connection on the vapourizer. The sample was held in a cup-like depression (approximate volume 0.25 mL) in the closed end of the sample holder. The assembly allowed the the sample to be positioned in the center of the extraction tube. A thermocouple placed within the hollow sample holder was positioned directly beneath the sample so that a digital thermometer (Analog Devices AD 2051) could monitor the temperature of the sample through out the experiment.

A gas diffusion bulb, six centimeters long and two centimeters wide, was incorporated into the sample holder halfway along the length of the rod. This was added to the sample holder to create a turbulent flow of ligand vapour in the sample region.

Chelate Trap

A collection tube was used to trap any volatile radioactive chelate that was formed, immobilize the metal and regenerate the ligand. The tube (10 cm long x 0.25 cm ID) was packed loosely with glass wool and the glass wool was saturated with ~ 1 mL of 85 % phosphoric acid. The acidified wool was dehydrated prior to use in a nitrogen stream (20 mL min^{-1}) at 150 °C to prevent the formation of nonvolatile hydrated ligands. During an extraction experiment the collection tube was held at 150±10 °C with a set point temperature controller (Omega Series 20). Hot chelate gases passing through the collection tube were broken down into the free acid ligands and the metal ions. The latter were trapped as their phosphates in the glass wool matrix. As added precautions, the exhaust gases were passed through a cold trap, (where the free ligand was condensed), and finally through a gas scrubber filled with dilute HCl prior to being released into a fume hood.

Sample Detection System

The amount of sample remaining in the sample cup was monitored throughout the experiment by a NaI(Tl) γ-ray detector (3 x 3 inch cylinder) coupled to a 1024 channel Multi - Channel Analyzer (MCA) (Canberra Series 30). The multichannel analyzer was operated in the external multichannel scalar mode with the channel advance and start dwell signals coming from the controlling computer. Throughout the experiment the lower level discriminator was set to exclude all signals below ~ 1000 KeV, thus enabling the detection of the two main iron- 59 photopeaks at 1099 and 1291 KeV but excluding the main background peak at 835 Kev from Mn-54. Spectra of the sample before and after extraction included the γ-ray spectrum from ~200 to 1400 Kev.

The detector was shielded from background activity by inserting it in an open ended lead cylinder 2 cm thick. Additional protection of 5 cm of lead was provided on one side of the detector to prevent detection of activity from the collection tube. The detector was also enclosed in a copper-mesh Faraday cage to protect the photomultiplier tube from magnetic fields in the experiment area.

Data Acquisition

Data acquisition was controlled by a microcomputer, using an interface board designed and assembled in this laboratory. The board was designed such that it was dependent upon the host microcomputer for programming, but after being programmed it could operate independently of the host computer.

Data request signals were generated by the interface board and sent to the digital thermometer at regular programmed intervals, usually ten seconds. The board also placed the MCA in the external multi-channel scaling mode. In this mode the channel advance and start dwell signals for the MCA originated on the board and were sent to the MCA at programmed intervals, simultaneous with the data request signal.

Data Reduction

The similarity of thermoradiometry to thermogravimetry should allow thermogravimetric models to be used for the kinetic analysis of TRG data. The fact that these reactions are not decompositions, but volatilizations, also allowed relatively simple models to be used.

The thermoradiometric data were analyzed using two computer programs, THERMAN and KINET. The program THERMAN allowed TRG data to be processed and displayed, and output processed data for the program KINET. The program KINET put the data received from THERMAN into the non-isothermal Arrhenius equation and fit the data to a best straight line (see Appendix A).

2.3 Commissioning of volatilization apparatus

The apparatus was tested to ensure that the design specifications were met.

The ligand delivery system was calibrated by measuring the volume of ligand delivered by the peristaltic pump.

The temperature controller for the extraction tube was tuned following the instructions of the manufacturer. After tuning, the control of the extraction tube temperature was tested by monitoring the sample holder temperature during a number of temperature ramps. The thermal stability of the apparatus was tested by heating the apparatus to a set point of 500 °C.

The efficiency of the chelate trap was tested by generation of the chelates as planned, but using non-radioactive samples. The intense red color of the chelates enabled their progress past the collection area into the cold trap, or further, to be visually monitored.

The complete apparatus and data analysis procedures were then tested by studying the volatilization and transport of a number of iron species using the two ligands H(hfa) and H(tfa).

Radioactive iron samples where produced by irradiation in a high flux site (5E) of the McMaster Nuclear Reactor. Sample lots (~10 mg) were sealed in quartz vials, irradiated for 48 hr at a power level of 2 MW and allowed to cool for 2-3 days prior to use. Working samples of ~ 2 mg were taken from these sample lots for study. Radiochemical purity of the bulk samples was determined using a high-resolution Ge(Li) γ-ray detector.

Powdered iron metal and iron oxide samples were irradiated and used directly. Iron chloride was produced from the action of HCl on the irradiated metal followed by drying at 150 °C in a stream of dry nitrogen. Iron sulfate was produced by repeated action of sulfuric acid on the chloride produced as above.

The ligands were obtained from Aldrich and were used as received.

Prior to volatilization, a γ-ray spectrum of assembled apparatus without sample was obtained. A sample was then placed in the sample cup and the sample holder returned to the apparatus. A second γ-ray spectrum was then obtained for comparison to a spectrum taken after volatilization and transport of the sample.

Volatilizations were usually done using a temperature ramp of 3.0 °C min^{-1}. The temperature controller was programmed to generate a linear temperature ramp between selected initial and final temperatures (T_i and T_f, respectively). The controller was set to raise the apparatus temperature from ambient to T_i and stay at that temperature for 10 minutes to allow the system to stabilize. After the controller started the ramp towards T_f, the ligand flow to the vapourizer and data acquisition were started. At the end of the ramp, after T_f had been reached, the ligand flow and data acquisition were halted and the apparatus was baked out at 450 °C for 10 min prior to allowing the apparatus to return to ambient temperature.

The integrated count and temperature data collected in a volatilization experiment were processed as described in Appendix A.

3. RESULTS

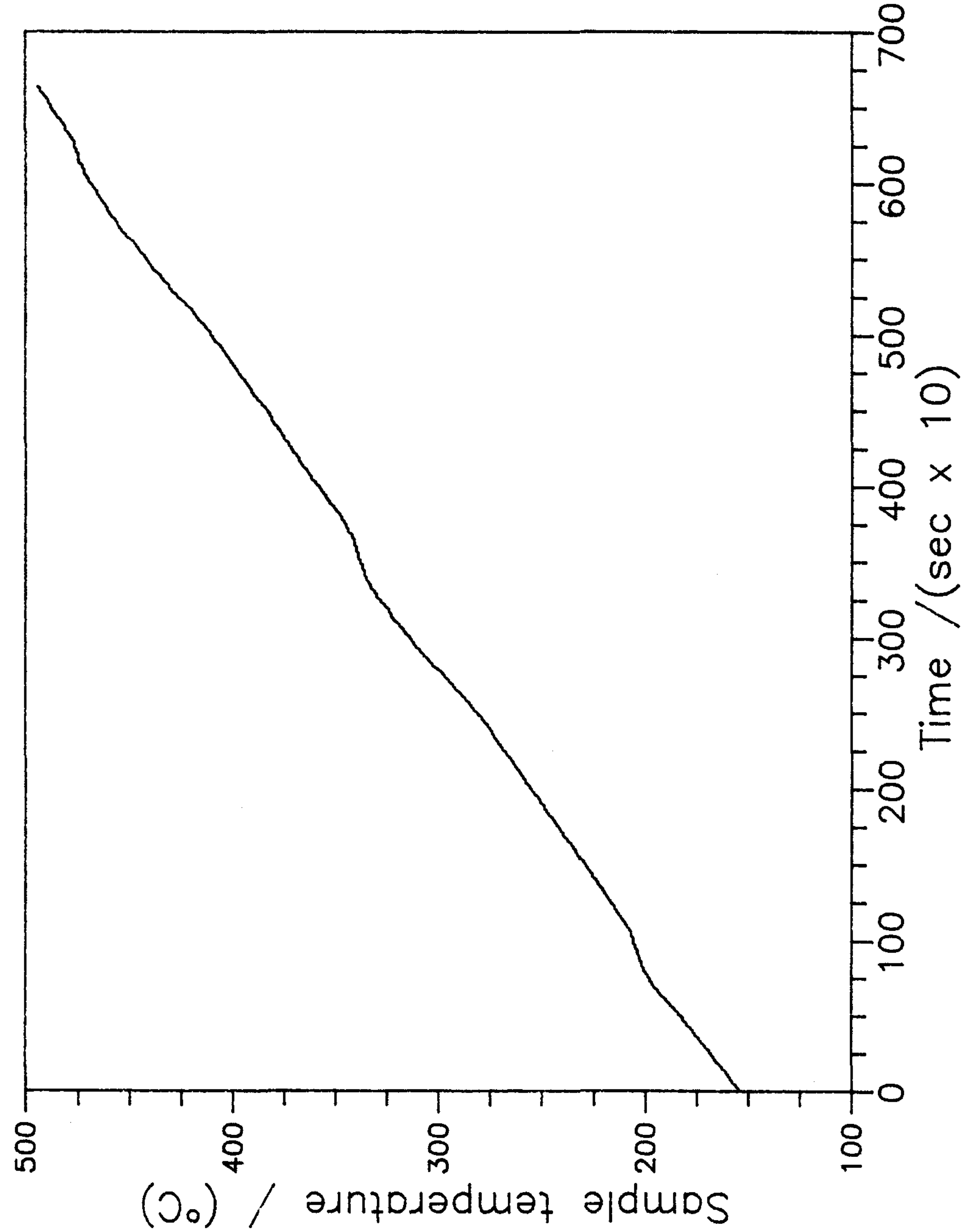
The results of the commissioning experiments indicate that the apparatus fulfills the design specifications.

Preliminary studies demonstrated that iron metal and ferric oxide reacted with gaseous H(tfa), producing visible quantities of the the volatile red chelate. These reactions were thought to be among the least favorable, and positive results at this point indicated that iron would be reactive enough in general for successful study. The chelates $Fe(hfa)_3$ and $Fe(tfa)_3$ are also completely volatilized at 120 °C and 180 °C respectively in thermogravimetric experiments at 10 °C min^{-1} [10]; this high degree of volatility ensured that the rate of loss of activity from the sample site was due only to the rate of formation of the chelates.

The sample temperature as a function of time was slightly non-linear (see Figure 3), however the temperature was within ±5 °C of programmed ramp temperature at programmed temperatures below ~480 °C. The apparatus was thermally stable when the sampling area was heated to 500 °C.

The chelate trap was effective as a means of immobilizing the metal ions after they had been volatilized

Figure 3 Sample temperature as a function of time



and transported. There was no visible evidence of the chelates breaking through the collection tube and condensing in the cold trap with the ligand.

These early results allowed further experiments with radiotracers to be attempted. After the iron samples were irradiated and allowed four days of decay, they were checked for radiochemical purity with a Ge(Li) γ-ray detector. Major photopeaks seen were from iron-59 (1099 and 1291 KeV) and manganese-54 (834 KeV). The ^{54}Mn was produced by the ^{54}Fe(n,p)^{54}Mn reaction,thus it was unavoidably present in all samples. No other major activity was detected in the samples. Tungsten-187 (686 KeV) was often detected in trace quantities, but it was not observed with the NaI(Tl) detector.

Gamma spectra of the complete apparatus, without sample (background spectrum), the apparatus with a sample before (sample spectrum), and after (result spectrum) extraction were obtained with a NaI(Tl) detector (see Figure 4). The apparatus exhibited a constant background activity from zinc-65 (1115 KeV) as the major feature. This contamination was inextractably adsorbed onto the glass of the apparatus and did not interfere with the monitoring of the change in iron activity, although it was not resolved from the main iron photopeak.

The major features of the sample spectrum were the two iron photopeaks (1099 and 1291 KeV) and the single

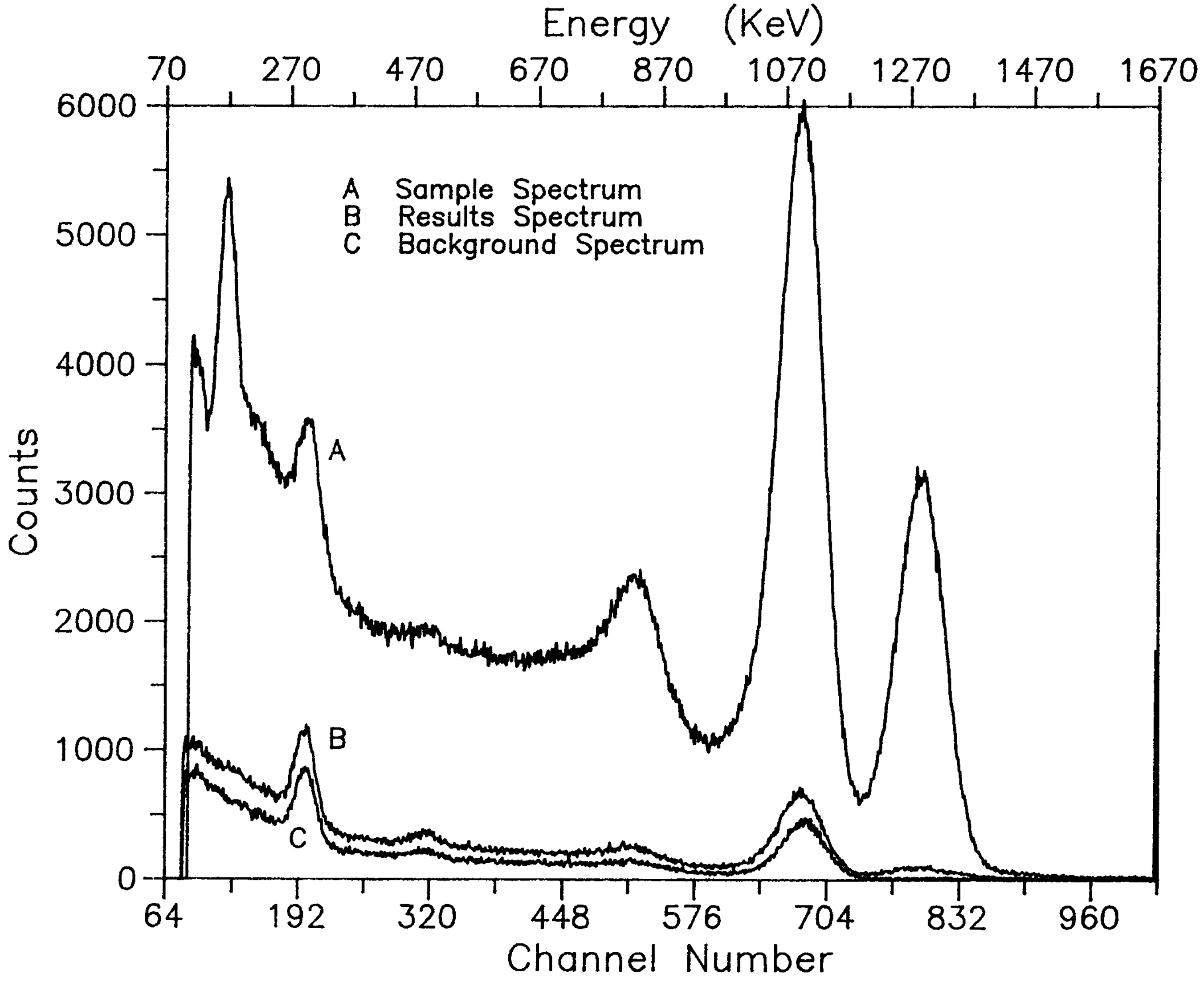


Figure 4 Gamma-ray spectra of volatilization apparatus

^{54} manganese photopeak. The resulting spectrum indicates that, for the experimental data shown, the extraction of iron was near to 98%. A large fraction of the manganese was also volatilized and transported. The interfering change in activity was excluded from detection during an extraction by setting the lower level discriminator at 1000 KeV. As a result, the Compton scattered iron photons were not counted and a large part of the total iron signal was lost.

Sample thermoradiograms (TRG), and the first derivative of the thermoradiograms (DTRG) for a variety of iron species and and the ligand H(hfa) are given in Figures 5 to 9. Similar thermoradiograms for H(tfa) are given in Figures 10 to 13. It is evident that the fluorinated pentanedione ligands, in particular H(hfa), are capable of the volatilization and chemical transport of various iron chemical species. Additionally, the extraction of very low levels of some species is possible, as is demonstrated by the volatilization of a large fraction of the ^{54}Mn (see Figure 4).

From the DTRG traces the volatilization threshold temperature (T_{th}) and volatilization rate maxima temperature (T_{max}) for a volatilization can be obtained. These values are given in Table 2 for the various iron species, and are

Figure 5 Ferric Chloride volatilized with H(hfa) at a ramp of 3°C min^{-1}

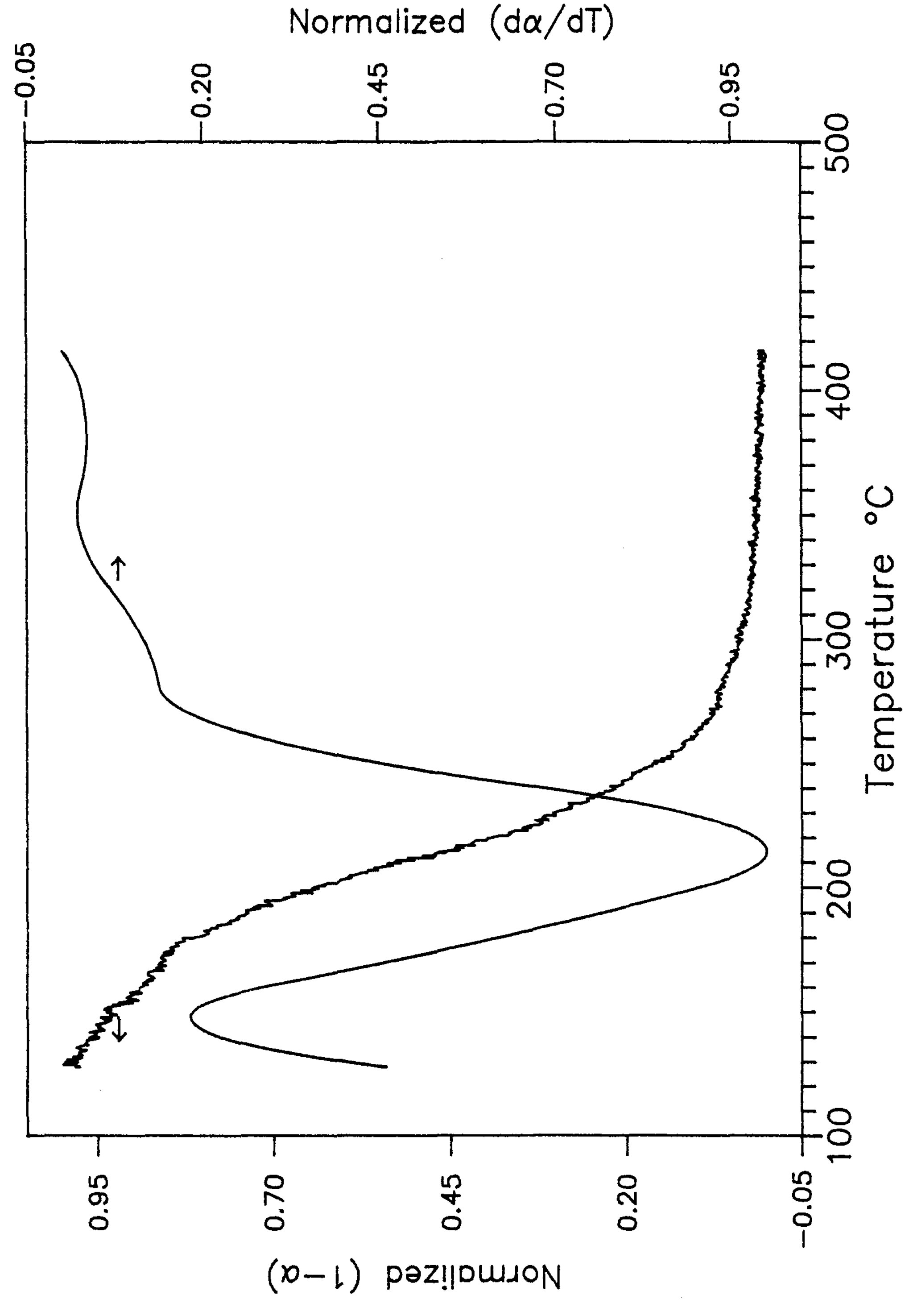
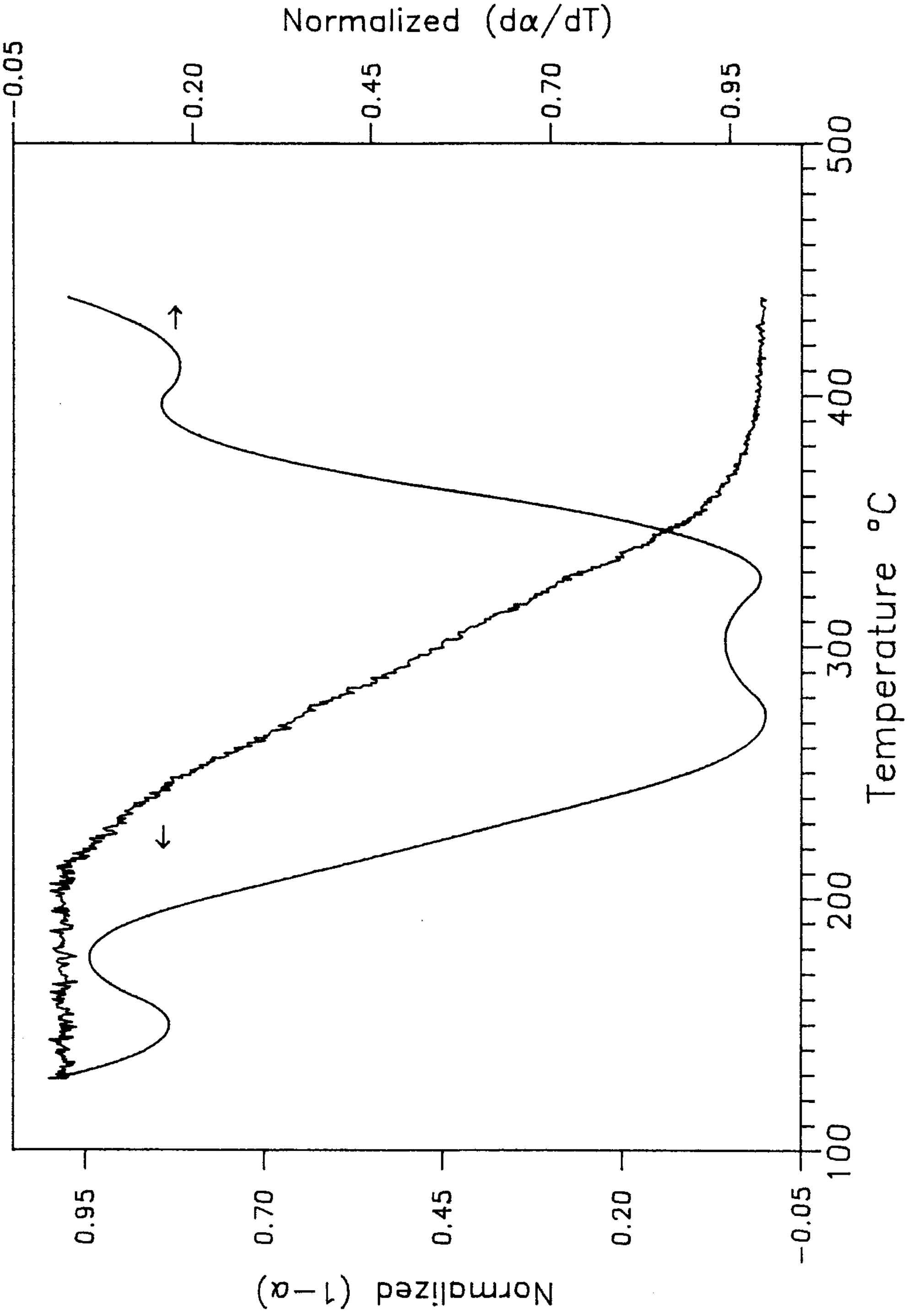


Figure 6 Iron Metal volatilized with H(hfa) at a ramp of 3°C min^{-1}



<u>**Figure 7 Magnetite volatilized with H(hfa) at a ramp of 3°C min^{-1}**</u>

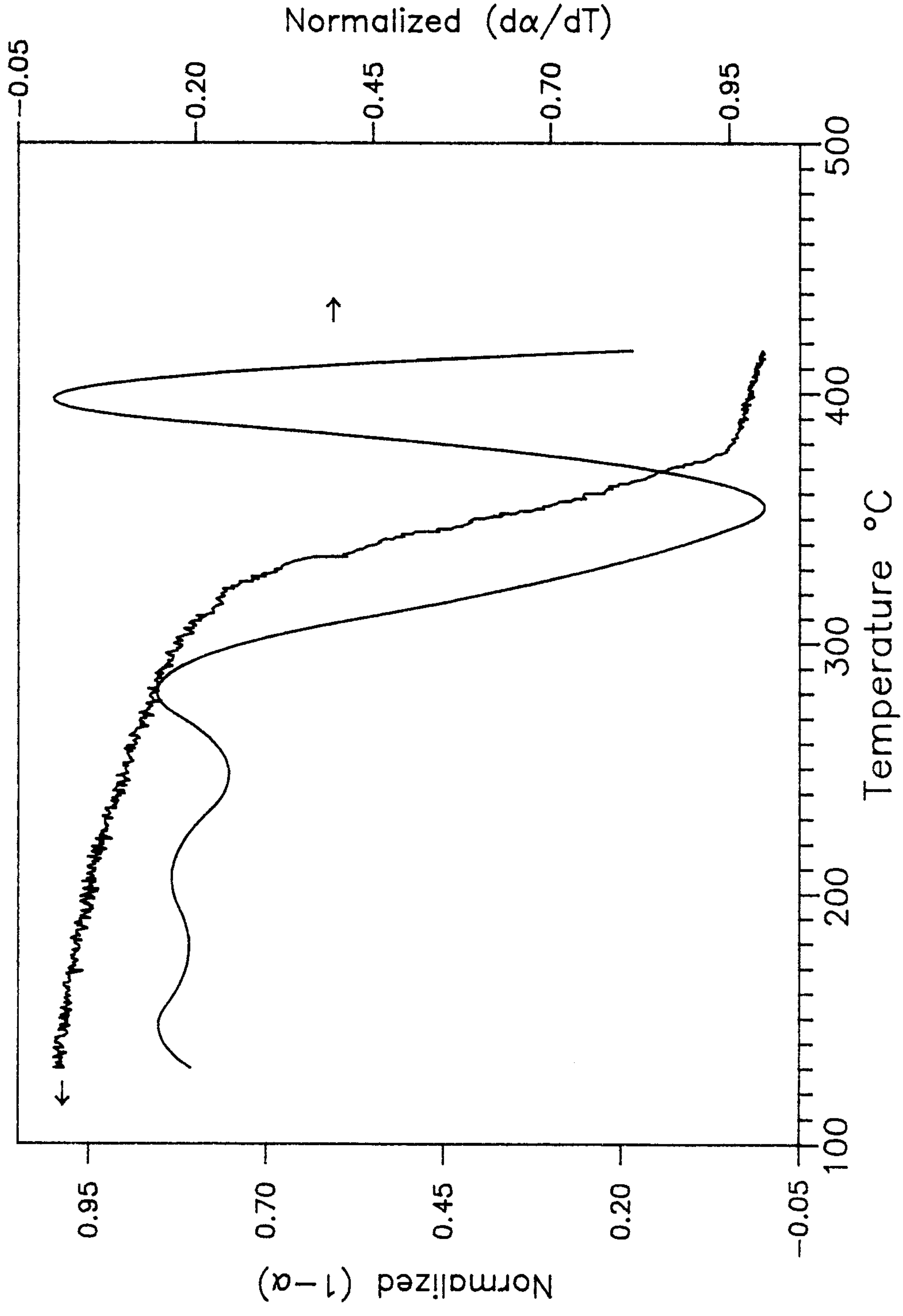


Figure 8 Ferric oxide volatilized with H(hfa) at a ramp of 3°C min^{-1}

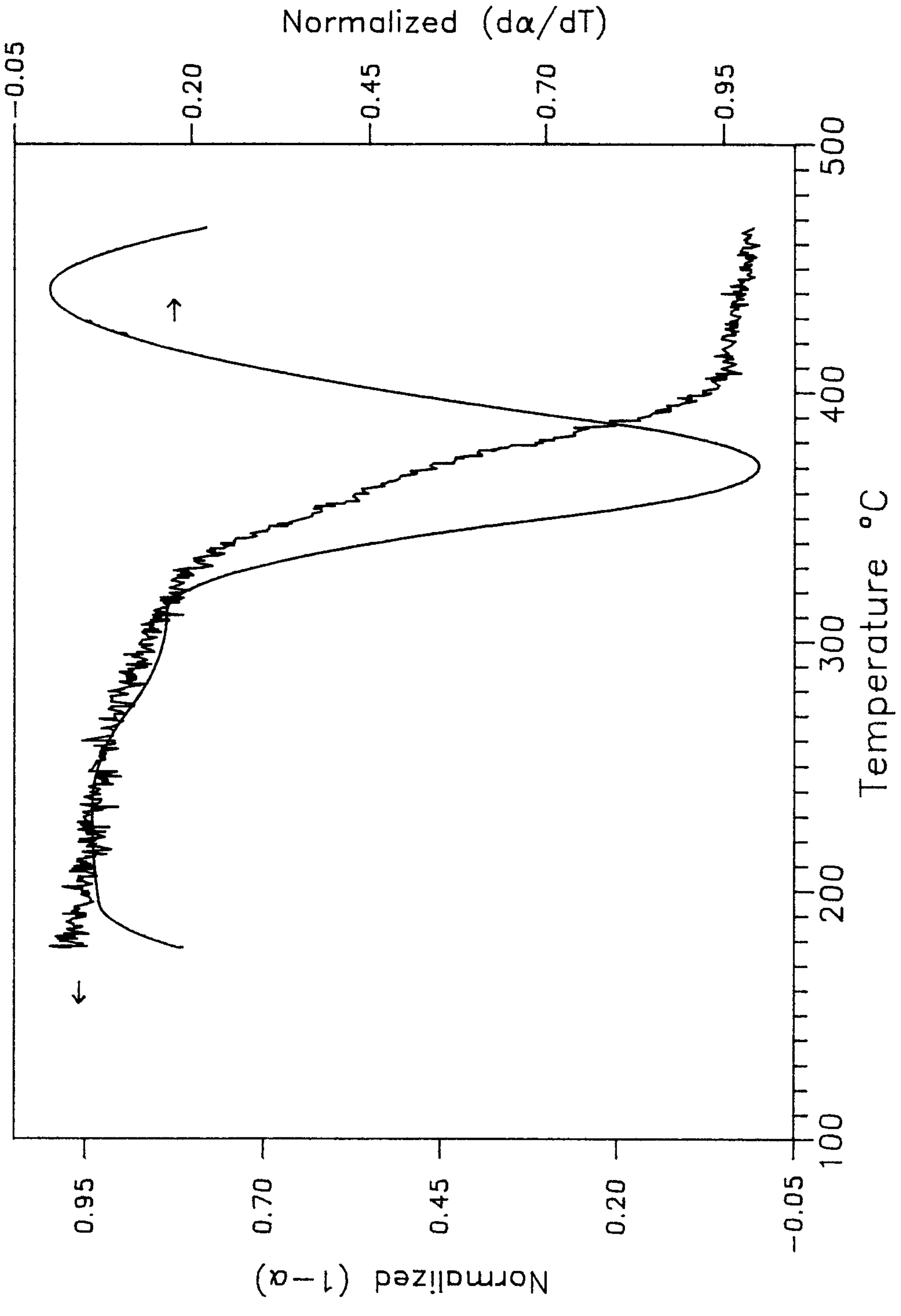


Figure 9 Ferric sulfate volatilized with H(hfa) at a ramp of 3°C min^{-1}

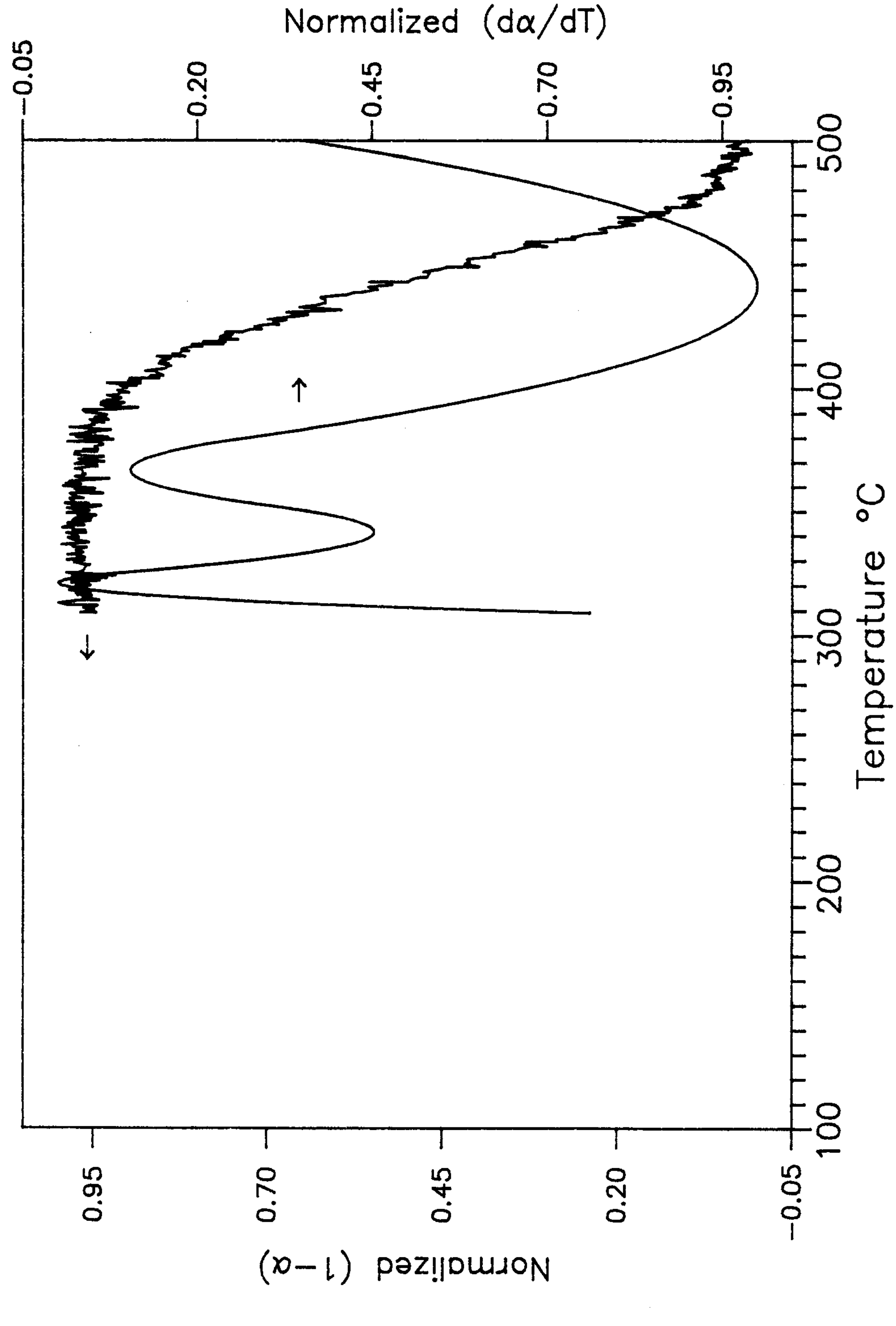


Figure 10 Ferric Chloride volatilized with H(tfa) at a ramp of 3°C min^{-1}

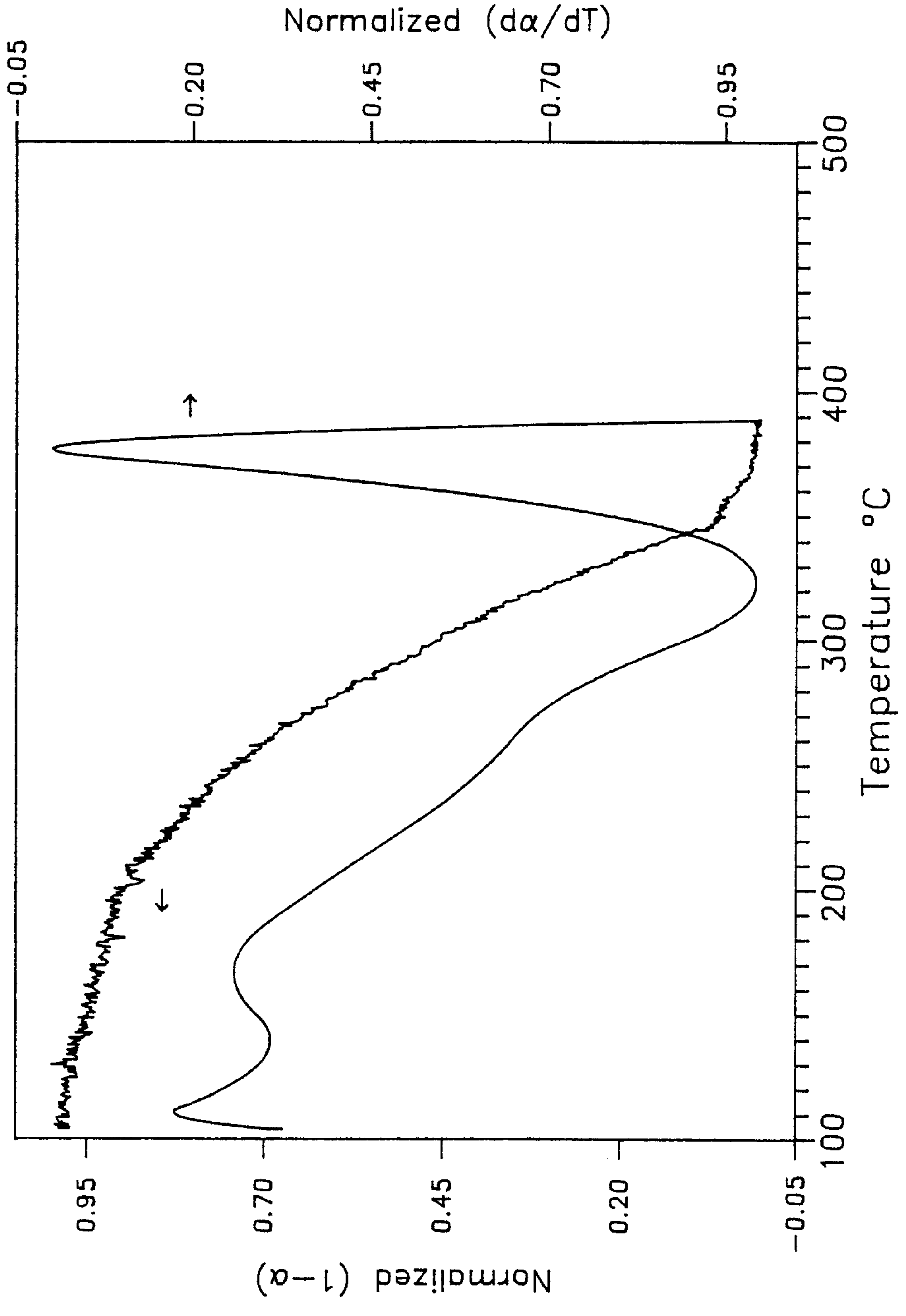
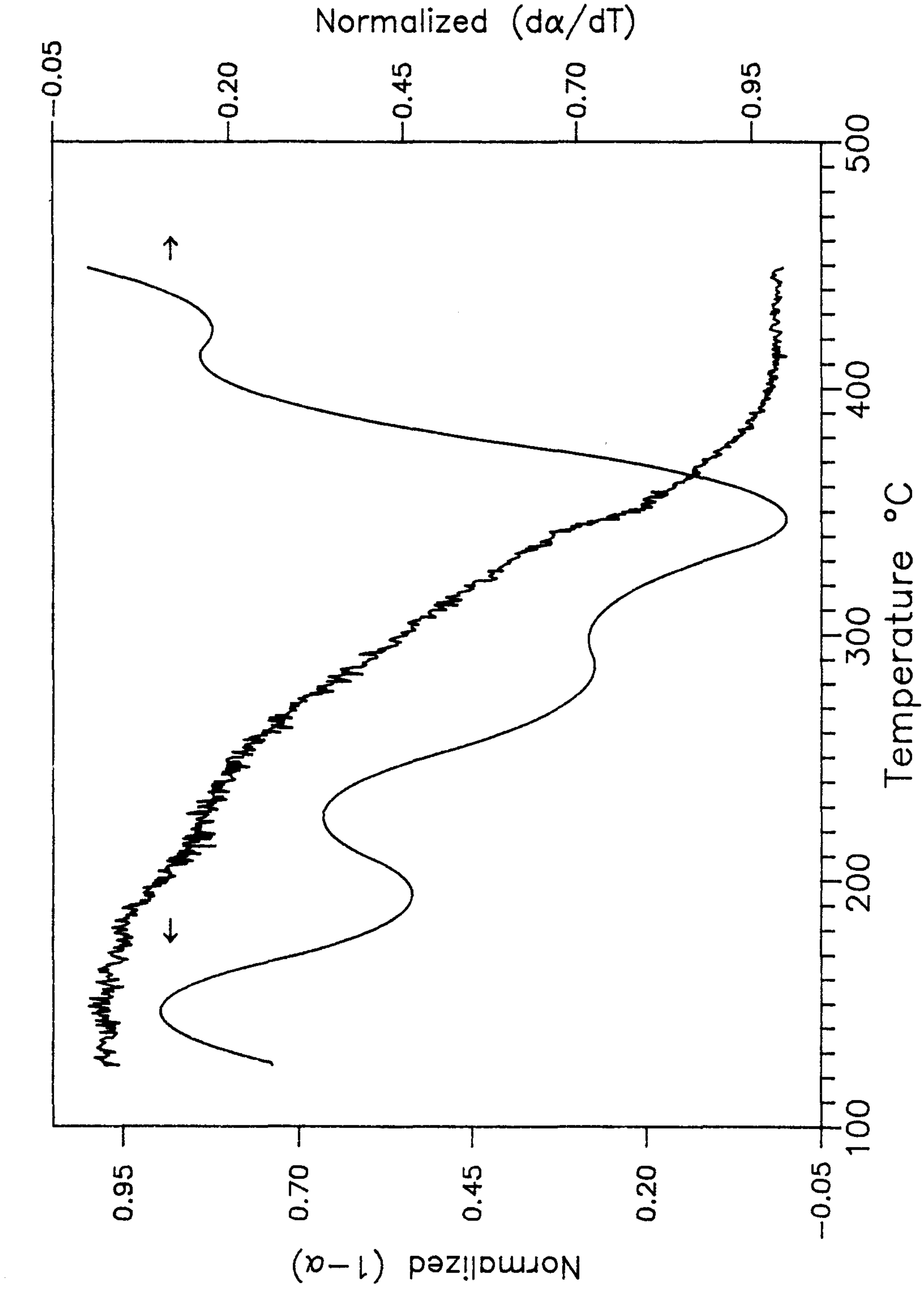


Figure 11 Iron metal volatilized with H(tfa) at a ramp of 3°C min^{-1}



<u>Figure 12 Magnetite volatilized with H(tfa) at a ramp of 3°C min^{-1}</u>

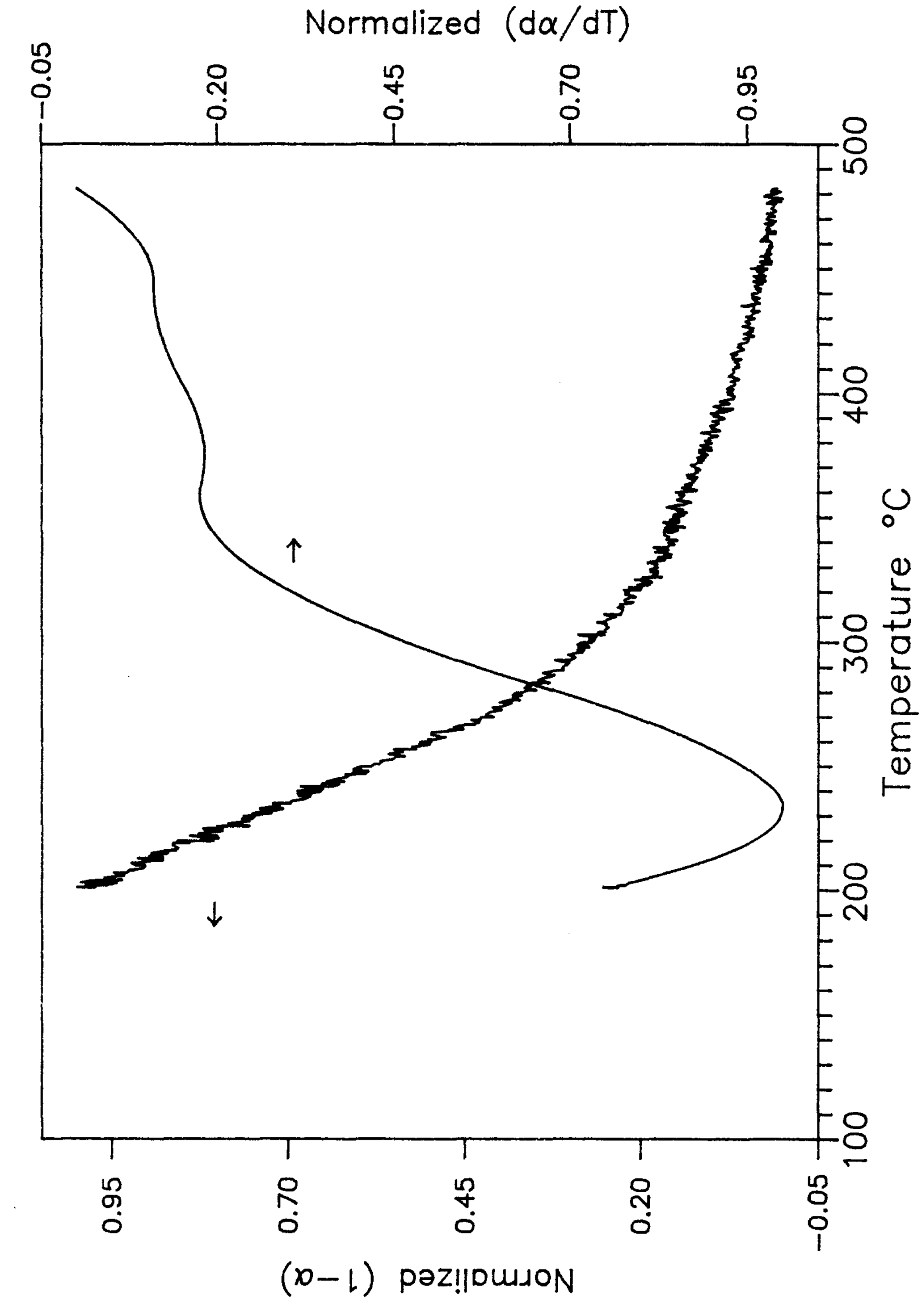


Figure 13 Ferric oxide volatilized with H(tfa) at a ramp of 3°C min^{-1}

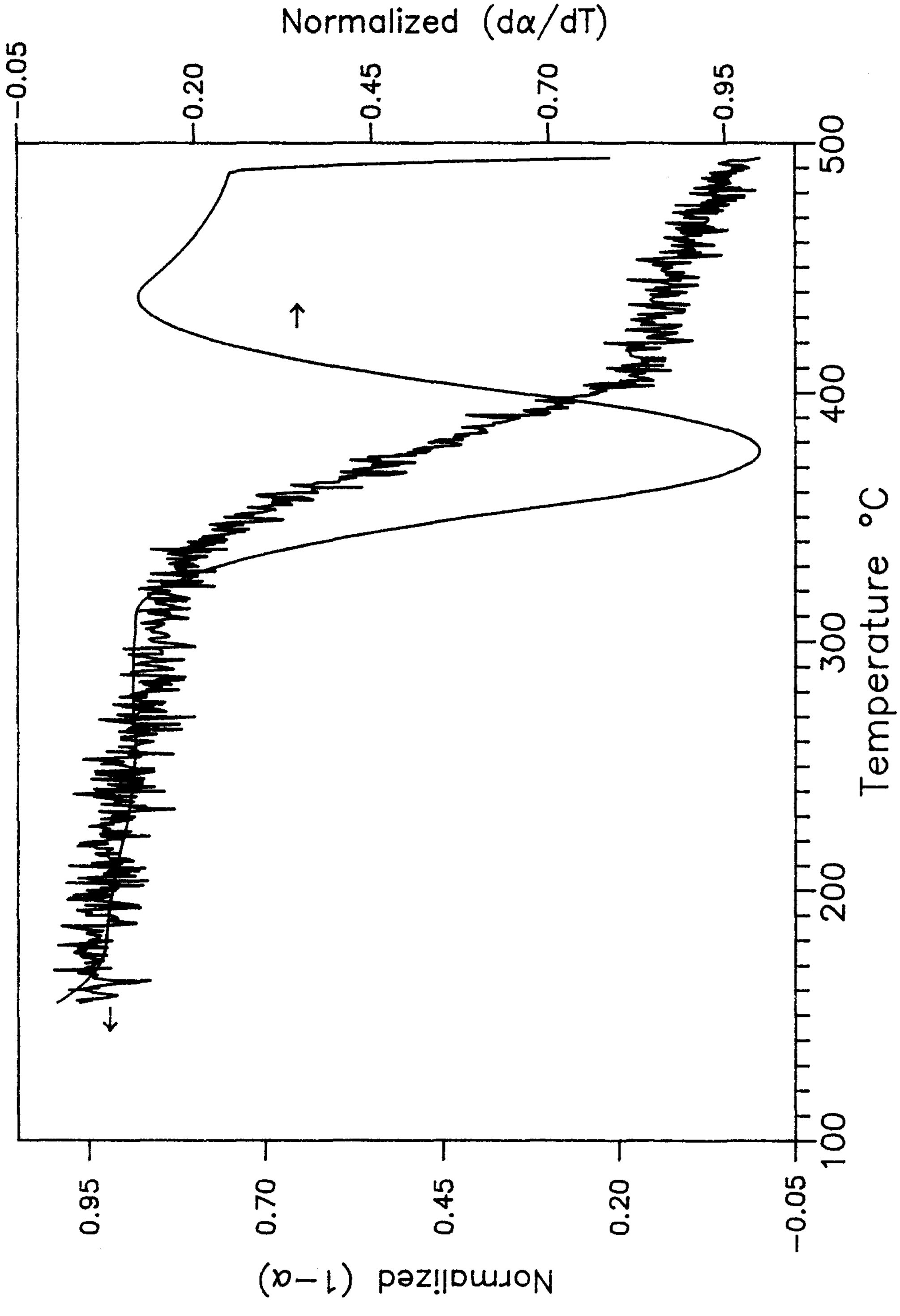


Table 2: Threshold Temperatures and Maximal Rate Temperatures for Single Species Extractions, 3°C min^{-1} ramp

a) Volatilizations with H(hfa)

Sample	T_{th}*		T_{max}*
chloride	148 ± 5		215 ± 6
metal	180 ± 6	a)	273 ± 8
		b)	327 ± 10
magnetite	286 ± 8		355 ± 10
ferric oxide	316 ± 5		370 ± 7
ferric sulfate	367 **		442 **

a) Volatilizations with H(tfa)

Sample	T_{th}		T_{max}
chloride	167 ± 4		321 ± 6
metal	215 ± 9	a)	269 ± 15
		b)	347 ± 10
magnetite	320 ± 6		375 ± 10
ferric oxide	340 ± 7		377 ± 12

* uncertainties given as one standard deviation of the mean

** result of one volatilization

dependent upon the initial chemical species of the sample volatilized.

As can be seen by Figures 5-13 the extraction of even single iron species did not give simple extraction curves. Iron metal shows two distinct peaks in the DTRG trace, and the extraction is quite drawn out compared to the other traces. The comparatively long volatilization of the metal may be due to the fact that the metal must be oxidized by the ligand prior to chelate formation, whereas other species are present in the ionic state. The two peaks in the extraction curve of iron metal cannnot be due to the differential extraction of iron allotropes present in the sample, as there is only one stable form of metallic iron (α-iron) below 906 °C [11]. Competing volatilization mechanisms also should produce additive peaks in the DTRG trace, not separate peaks as are obtained. The multiple peaks observed may be due to impurities, however the relative magnitudes of the peaks suggests that this is also unlikely.

Magnetite, which might be expected to give two peaks in a DTRG trace, one each for the ferrous and ferric components, produces a single sharp peak (Figures 7 and 12). This result is also obtained when the magnetite is volatilized at a lower (1.5 °C min^{-1}) heating rate (see Figure 14). The DTRG traces indicated that the magnetite curves were distinct from the ferric oxide traces for both

H(hfa) and H(tfa) extractions (Figures 8 and 13).

The reproducibility of extraction curves from replicate samples was generally quite good. For extraction of single species the TRG traces were similar (see Figure 15) and the DTRG traces were reproducible (see Figure 16) as were values for T_{th} and T_{max} (see Table 3). There are a number of possible causes for the variation in the extraction curves, the most probable ones being variation in the sample size and the slightly non-linear temperature ramps used for extractions.

The results from mixed samples were generally complex and the differing species were not always completely resolved under experimental conditions, although multiple extraction steps were usually distinct in the derivative traces. Different components were identified by their approximate T_{th} and/ or T_{max} values, as the overlapping of the volatilization reactions usually resulted in the shifting of the DTRG peaks.

Volatilization of mixed species were reproducible as as shown in Figure 17. The difference in the two volatilizations are due mainly to the larger sample size (~37 %) of A. These volatilizations gave two or more distinct reactions in the derivative traces. The results from mixed species volatilizations were anomalous in that the T_{max} values for both species were generally lower, and the volatilizations usually proceeded to a greater extent.

Figure 14 Magnetite volatilized with H(hfa) at a ramp of 1.5°C min^{-1}

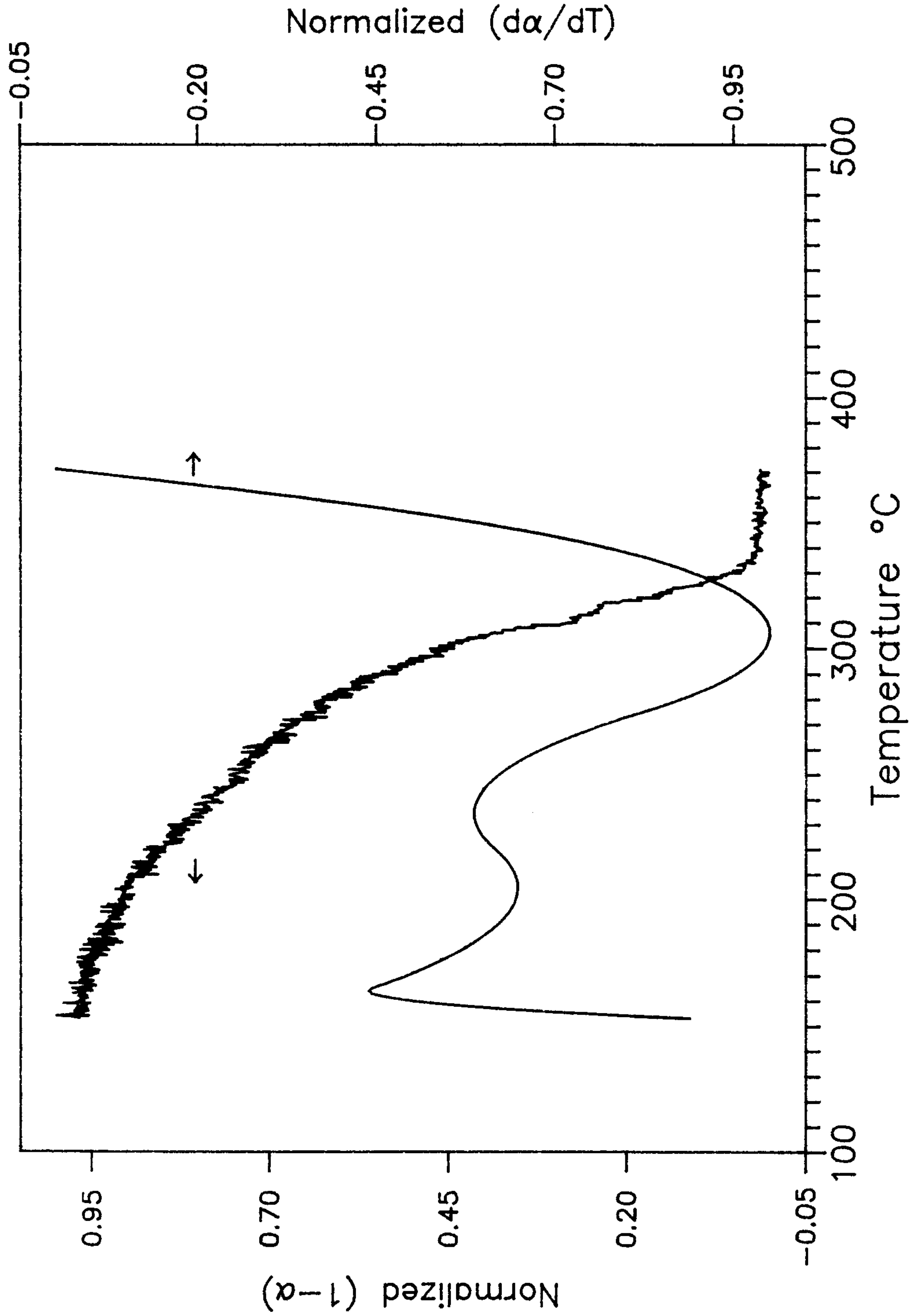


Figure 15 Replicate extractions of iron Metal with H(tfa) - TRG traces

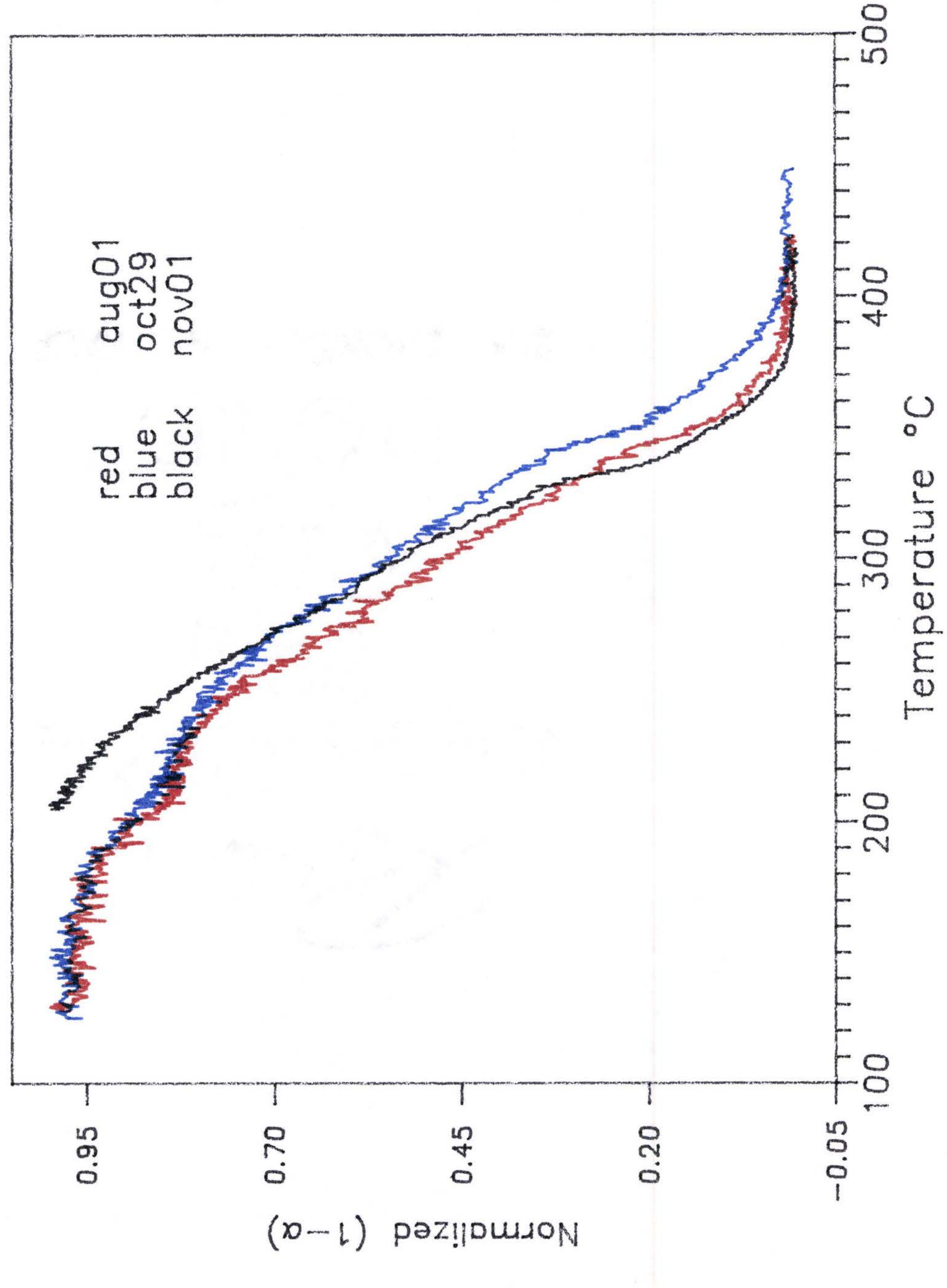


Figure 16 Replicate extractions of iron Metal with H(tfa) - DTRG traces

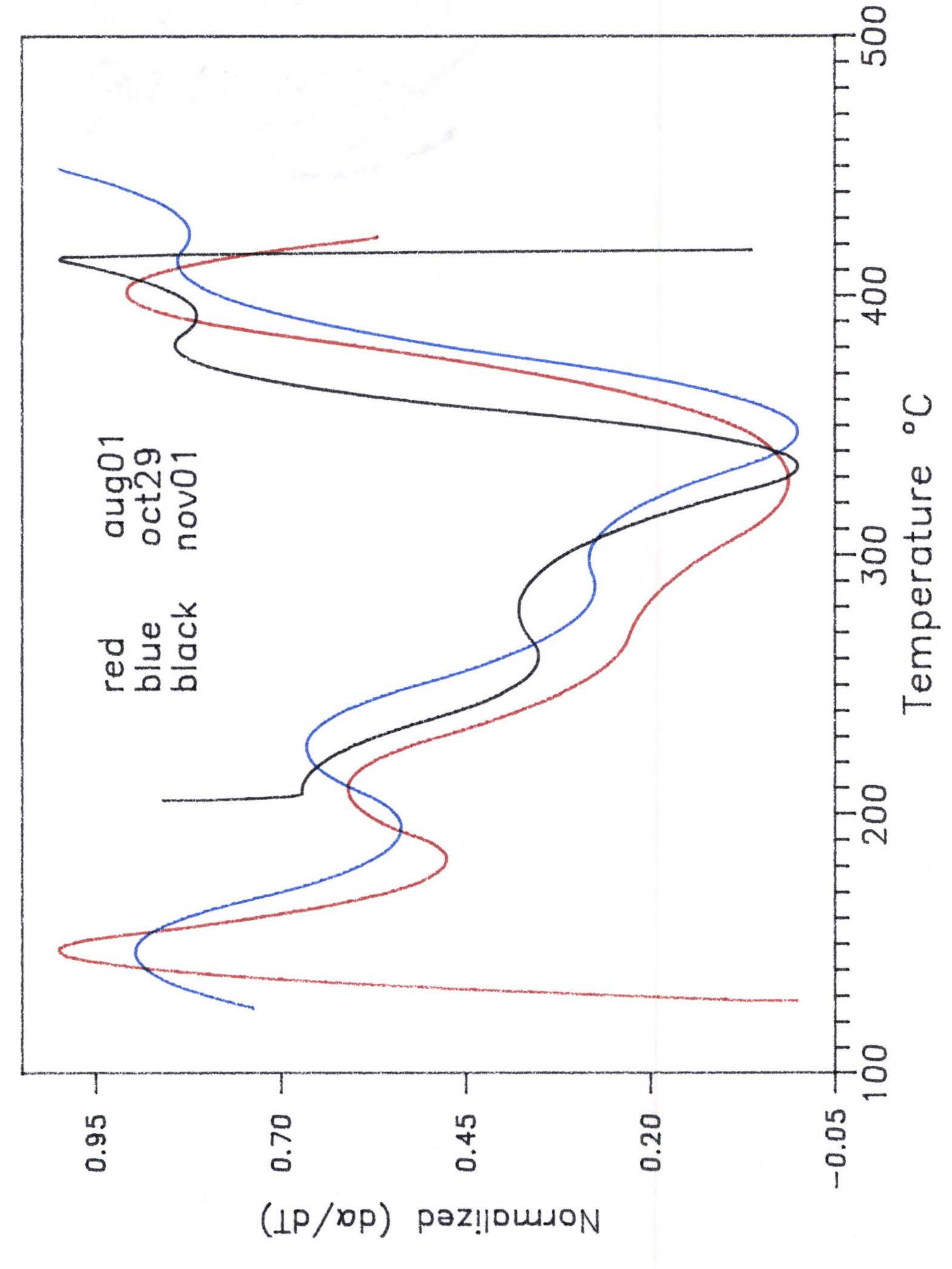


Figure 17 Volatilizations of Iron metal and magnetite with H(tfa) at a ramp of 3°C min^{-1}

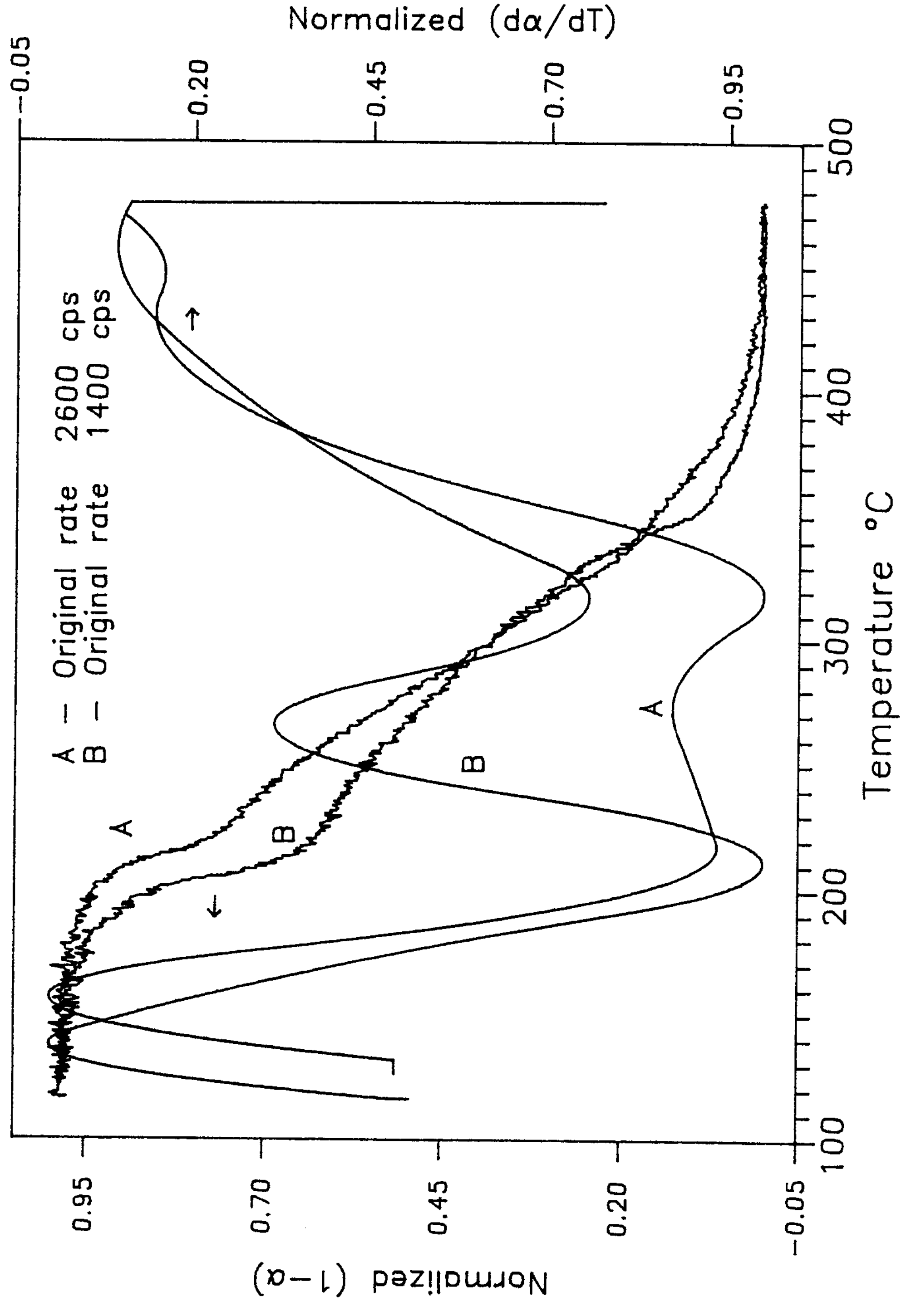


Table 3: Comparison of Threshold and Rate Maxima Temperatures for Repeat Extractions

Sample*	T_{th}	T_{max1}**	T_{max2}**
Aug01	211	261	334
Oct29	210	260	328
Nov01	226	287	347

* Samples were iron metal volatilized with H(tfa) using a ramp of 3°C min^{-1}. Samples were subsets of the same lot.

** As noted in the text, iron metal exhibits two reaction rate maxima, here denoted as T_{max1} and T_{max2} for the first and second rate maxima respectively.

As is shown in Figure 17, the extraction of equal activities of iron metal and magnetite with H(tfa) the T_{max} values obtained are 210 °C and 320 °C, lower than the 280 °C and 375 °C obtained for iron metal and magnetite respectively in single samples. The reaction extent was also enhanced from the expected value of 70 % to 90 % and 96 % for the two extractions.

Other systems behave in a similar manner, such as the ferric chloride - ferric oxide H(hfa) (Figure 18), which gives two peaks in the DTRG trace, at 205 °C and 330 °C, verses the values of 215 °C and 370 °C obtained with single samples. The extent of the volatilization, at 88% was also slightly higher than the expected value of 80%.

3.1 Thermal Analysis Results

From the program THERMAN, the threshold and rate maxima temperatures (T_{th} and T_{max}) for the reactions under study could be obtained. These values are obtained from the inflection point at the beginning of the volatilization and the minima of the $d\alpha/dT$ curve respectively. These values were found to be characteristic of the species being volatilized (Table 2).

From the non-isothermal Arrhenius analysis program KINET, values for the activation energy and frequency factor where obtained (see Table 4). The correlation coefficient

Figure 18 Volatilization of ferric chloride and ferric oxide with H(hfa) at a ramp of 3°C min^{-1}

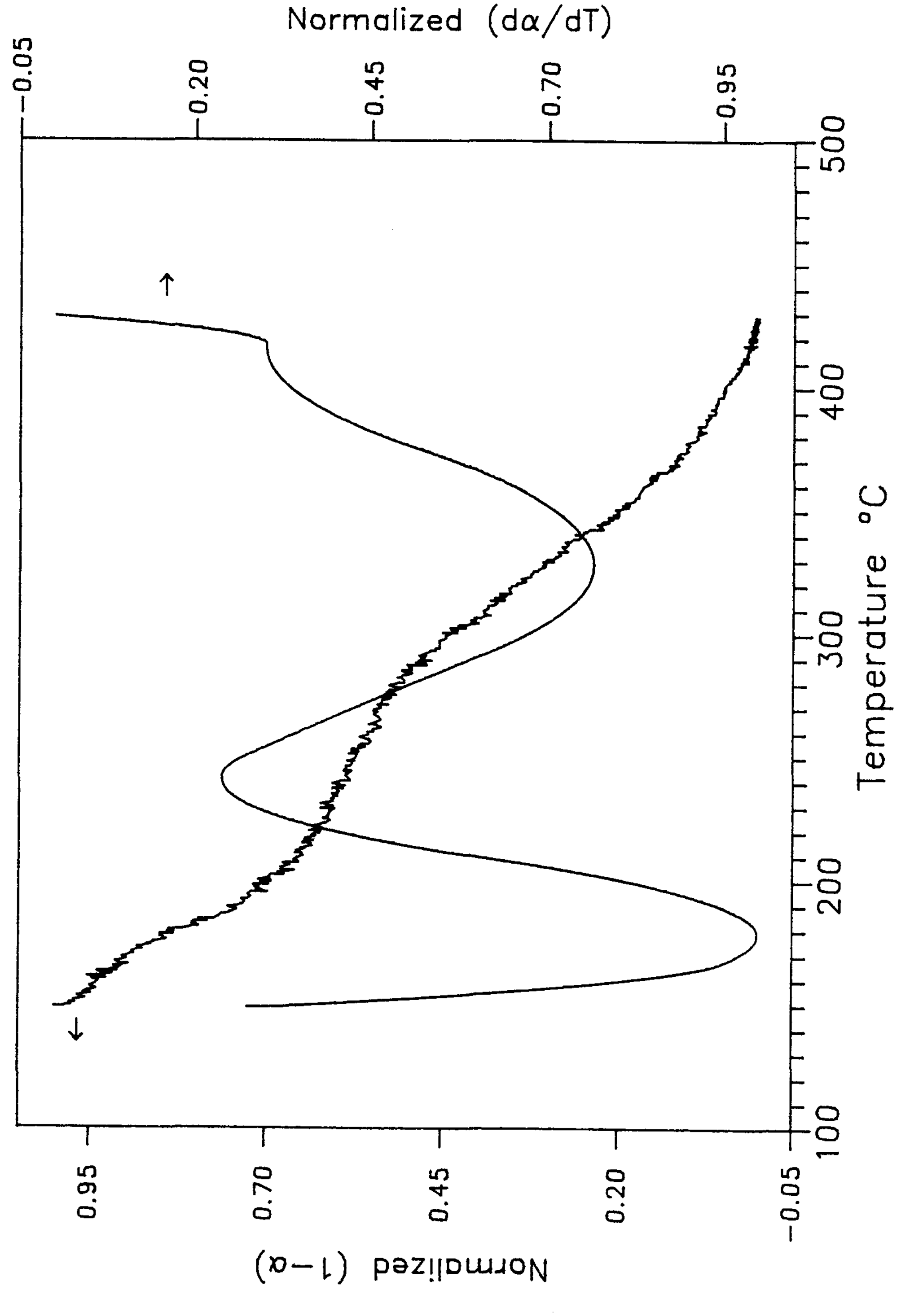


Table 4: Results from the Non-Isothermal Arrhenius Analysis Program KINET

a) Volatilizations with H(hfa)

sample		corr of line	Ea 1000 kJ/mole	A seconds	Fraction volatilized
chloride		0.997	5.46	3.5E+3	1.0
metal	a)	0.993	49.2	2.0E+6	
	b)	0.993	76.9	4.2E+8	1.0
magnetite		0.997	15.1	3.2E+10	0.92
ferric oxide		0.992	12.7	1.1E+8	0.50
ferric sulfate		0.996	10.3	1.6E+5	0.50

b) Volatilizations with H(tfa)

sample		corr of line	Ea 1000 kJ/mole	A seconds	Fraction volatilized
chloride		0.991	42.4	2.1E+1	0.96
metal	a)	0.997	39.0	9.2E+0	
	b)	0.995	69.1	6.5E+3	0.90
magnetite		0.983	21.8	4.1E-1	0.38
ferric oxide		0.956	78.7	9.46E+3	0.30

of the best straight lines were generally good, above 0.990, for data sets that usually spanned greater than 50 °K. The analysis with lower correlation were those of volatilizations which did not go to completion, resulting in α values with a larger degree of uncertainty.

The general form of the nonisothermal Arrhenius analysis does not specify the value of n in equation (6), although there is theoretical justification only for orders of 0,1/2,2/3, and 1 [7]. The program KINET incorporated a loop allowing various specified values of n to be evaluated individually, and results of least squares analysis to be reported for each value of n. In all cases no significant advantage was gained by using a value of n other than 1.

Each species displayed one dominant reaction, with the exception of iron metal, where two reactions were found. The general trend of the E_a values, with H(hfa) values lower than those for H(tfa), with the exception of the two iron metal reactions, is what would be predicted considering the relative reactivity of the two volatilization agents.

The values for the activation energies obtained from the nonisothermal Arrhenius analysis, although exhibiting a large degree of variation, also demonstrate the increased reactivity of the more fluorinated ligand.

4. FUTURE WORK

The purpose of this work was to design and build an apparatus suitable for the study of the volatilization of metal species with β-diketone ligands. This work could lead to the development of a method for the speciation of trace metals in air particulate samples. Now that the general feasibility of this method has been shown, extensive future work is needed prior to this technique being generally applicable.

As this project did not envision real analysis by radiotracers, a general method of chelate analysis would be necessary. For analysis of trace metal species, volatilization followed by off-line determination is usually preferable to an on-line determination, as the on-line detection signal will be broad [1]. Thus a suitable method of chelate collection and and analysis will have to be developed.

The volatile chelates could be collected for subsequent off-line analysis by adsorption or condensation onto a suitable substrate such as polyurethane or silica gel. This would leave the chelates immobilized but still in a convenient form for analysis. The chelates could be revolatilized or taken up in an organic solvent for off-line determination.

After the generation and trapping of the chelates, there are a number of established techniques for quantitation. Extensive work has already been published on the determination of trace metals by gas chromatography of their H(tfa) or H(hfa) chelates [12], using an electron capture detector or atomic absorption as an end detector. The volatile chelates have also been used to introduce metals in an argon stream into an inductively coupled plasma [13].

Additional work is necessary on other metals commonly found in air particulates, such as lead, manganese, and vanadium, many of which are not amenable to study by radiotracer methods, as their neutron cross-sections or their half-lives are unsuitable. Studying the volatilization of these metals would involve the use of a thermobalance which has been designed or modified for use with the corrosive ligands used for volatilization.

Additional work with ligands other than H(hfa) and H(tfa) is also warranted. Other highly fluorinated β-diketone ligands, such as 1,1,1,2,2,3,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (H(fod)) may be useful for volatilizations requiring high temperatures on account of the increased thermal stability with higher fluorination.

Preliminary work with sulfur analogs of the β-diketone ligands, such as monothiotrifluoroacetylacetone and dithiotrifluoroacetylacetone has been done in our laboratory. These ligands appear to preferentially volatilize soft acid metals such as lead, cadmium and zinc. Further work would be necessary to determine the general applicability of these ligands, as they appear to have poor thermal stability relative to the diketones. If these ligands prove to be applicable to trace metal volatilizations they should be complementary to the diketone ligands.

The volatilization reactions of mixed species samples will have to be studied in greater detail. Results obtained to date indicate that these samples may not volatilize as the simple sum of the single species reactions. The behaviour of these types of samples will have to be understood if sample speciation is intended.

Finally, real samples would have to be run. The project was initiated with air particulate analysis, especially iron particulates associated with the steel industry in mind. The basis for iron particulate speciation was to determine the source (i.e., foundry or ore stock) of iron-bearing air particulate matter.

Problems expected with real samples are complex matrices with low levels of the element of interest, and the possible occlusion of a species in the bulk matrix. This may give some indication of the degree of bioavailability and hence environmental risk of the element of interest.

5. CONCLUSION

An apparatus has been designed and constructed to study the low temperature volatilization of solid iron species with the fluorinated pentanedione ligands H(hfa) and H(tfa). The apparatus was commissioned and a variety of iron species were successfully volatilized.

The rate of volatilization of the iron species was found to be dependent upon both the ligand used and the iron species. This method may provide a means for the speciation of iron in solid samples, such as air particulate samples.

APPENDIX A

Data collection and reduction

Data collection

The data obtained from TRG experiments consisted of two data arrays, temperature and integrated counts.

During a volatilization the integrated count data was collected and stored by the multi-channel analyzer, which could collect and store up to 1022 individual data points. After the experiment was finished, the contents of the MCA memory were transferred to a microcomputer for processing.

Temperature data was sent directly to the microcomputer during an experiment by the AD 2051 digital thermometer. The data was stored in memory for the duration the experiment, and written to disk at the end of the data collection step. Data request signals sent to the digital thermometer were simultaneous with channel advance signals sent to the MCA, this enabled temperature and count values to be correlated.

The raw data files were filtered prior to being used by the data reduction programs. Temperature files were parsed to remove extraneous sign and leading zero characters sent by the digital thermometer. Count files were parsed to remove ASCII control characters used by the MCA, and unnecessary (empty) channels were edited out to reduce the size of the data files.

Data Reduction

The count and temperature files were read by THERMAN, and were processed to allowed count data to be manipulated and displayed as a function of temperature.

For determining the kinetic parameters E_a and A, the activity values were normalized to range and stored as $(1 - \alpha)$. The first derivative of the α vs T data was computed numerically by means of a fourth order cubic spline on 15 breakpoints using the algorithms of DeBoor [14]. These algorithms used a piece-wise polynomial approach to fit the data, which was computationally efficient but tended to exaggerate the derivative at the boundaries.

After generation of the first derivative, the α and $d\alpha/dT$ curves were displayed, and a range was selected by the operator over which the volatilization rate was significant. The program THERMAN created an output file consisting of the values for T, α, and $d\alpha/dT$ for each point in this range. Typically 150-250 points were generated.

The output file generated by THERMAN was used by the program KINET as input. The values of T, α, and $d\alpha/dT$ at each point are put into the non-isothermal Arrhenius equation (see equation 6) and a least squares analysis was done on the resulting set of data points. The program allowed for the use of varying values of n, optionally displaying the data points and the best fit line and reporting the values for E_a and A for each value of n. If the data produced non-linear results at high or low values of α, as a result of low reaction rates, the analysis was performed on a subset of the original data.

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