

Final Report

Magnitude Assessment of Free and Hydrated Limes Present in RPCC Aggregates

ODOT Project No. 14676(0)

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Disclaimer Statement

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Ohio Department of Transportation or the Federal Highway Administration. This report does not constitute a standard, specification or regulation.

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Chapter 1

Introduction

1.1 Statement of the Problem

Earlier research [1] on recycled Portland cement concrete (RPCC) precipitate potential indicates that aggregates obtained from concrete pavements and recycled, as base or subbase aggregates in pavement will produce tufa. In this research, two RPCC samples from different sources were analysed for their tufa precipitate potential. A leachate study on these samples showed that one of the two RPCC samples produced tufa. Furthermore, the tufa has been observed in selected area of highways in Ohio blocking the drainage system [2].

Tufa occurs as a natural material and is considered a sedimentary rock composed of calcium carbonate. It is formed by precipitation from water that is rich in calcium ions and dissolved carbon dioxide. The sources of the calcium ions can be listed as the surface layer of concrete, and the sub-base and base of rubbelized calcitic limestone, dolomite, or Recycled Portland Cement Concrete (RPCC). The calcium ions present in these materials will dissolve in the acidic water. Also in the case of dolomite, there is a tendency to dissolve out magnesium ions in the acidic water. A reversibility of the acidic conditions caused by evaporation, escape of carbon dioxide, freezing, or certain combination of these conditions, will lead to a reduced solubility of the calcium ions thus leading to precipitation of calcium carbonate as tufa.

There are two possibilities of tufa formation; in one case the precipitate may be nucleated from a suitable surface, usually the concrete structure of the drainage system. The particle growth will occur as in the cave formation of stalactites and stalagmites. Such growth from the surface will lead to eventual blockage of the drainage system. In the second case, nucleation may occur in solution and result in the formation of free

flowing particles that may pose no immediate danger of blockage. An intermediate case may be postulated as the formation of a gelatinous precipitate of calcium carbonate. It is probable that such an event would transform into the first case noted above and eventually cause blockage of the drainage system. Also it is possible that free flowing particles present in the drainage system may form the nucleation surface and be cemented together causing blockage of the drainage system.

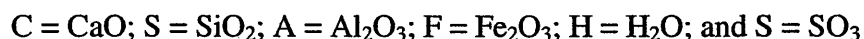
In summary, dissolution of calcium ions is possible from portlandite $[\text{Ca}(\text{OH})_2]$ formed on hydration of the Portland cement. It may also occur from calcite $[\text{CaCO}_3]$, dolomite $[\text{CaMg}(\text{CO}_3)_2]$, slag, or from the small amounts of free lime $[\text{CaO}]$. These materials may be present as minerals in aggregates in the concrete or mortars. Thus the use of old concrete rubble known as rubbelized RPCC as the base or sub-base in road construction may have the potential of precipitation as tufa. It should be noted that, in Ohio, dolomitic or calcitic limestone are frequently used to make concrete. The present study is confined to an examination of rubbelized RPCC and the magnitude assessment of free and hydrated limes that may produce tufa. The research study will serve as an aid to the decision of using RPCC as a base or subbase aggregates.

1.2 Chemical Process of Cement Hydration in Concrete

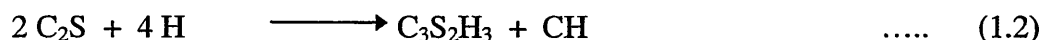
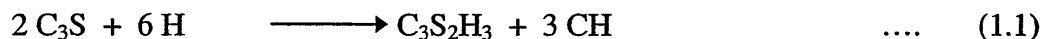
Cement clinker is manufactured by the heat treatment of limestone $[\text{CaCO}_3]$ with clay in a rotary kiln at a temperature of 1300-1500°C. The product is in the form of small, rounded lump called cement clinker. The cooled clinker is mixed with small amounts of gypsum $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$ and grounded to fine particles to provide cement. The gypsum has the property to control the rate of setting in the presence of moisture. In the absence of gypsum the setting would be very rapid. A hydration process takes place when water is added to cement powder [3]. This mixture of cement powder and water forms the basis of the hydration process where the development of strength in such “hardened cement paste” is a practical measure of the effect of hydration. Such tests are usually spaced out over 28 days but the hydration process can continue for a much longer

period. The hydration is a rapid process lasting a few hours, and then a dormant period occurs, where there is a temporary cessation of the hydration. It is then followed by a slow continuation of the hydration process which can be monitored in the thermal analysis experiments as an increase in portlandite production using Thermo-gravimetric analysis (TG). This slow hydration process can be followed by calorimetric experiments, as hydration is an exothermic process. The formation of the portlandite during the hydration process can also be followed using X-ray powder diffraction methods. The strength of the hardened cement paste is determined by the water to cement ratio and is paralleled by a decrease in porosity. In concrete, aggregates designated as “coarse” or “fine” are added. In Ohio the aggregate used in concrete is dolomite, calcite, quartz [SiO₂], and sometimes slag.

The four main components of the Portland cement clinker are tricalcium silicate (C₃S); dicalcium silicate (C₂S); tricalcium aluminate (C₃A); and a ferrite solid. The composition of ferrite solid varies between C₂F and C₆A₂F often represented as C₄AF. This notation is a convention used by cement scientists as:



An approximate representation of the hydration process for C₃S and C₂S is:



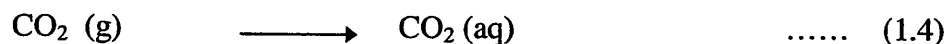
The C₃S₂H₃ is often represented as C-S-H indicating its amorphous nature and variable composition. Some authors refer to it as tobermorite gel. The hydration products of the other cement components- the calcium aluminosilicates are not generally described as producing CH.

Thermodynamic data [4] indicates that the solubility of silicate compounds is much lower than those of carbonates and hydroxides. Thus CH may be the more likely Ca^{2+} donor than the C-S-H or the hydrated aluminosilicates [5]. The calcium ions produced in acidic water (considered here as CO_2 dissolved in water) could be leached from portlandite, dolomite, calcite, and slag present in the RPCC. Over a period of 30 years (the rough age of the rubbelized RPCC from old concrete pavements), the portlandite formed initially will have undergone considerable carbonation through direct interaction with atmospheric carbon dioxide.

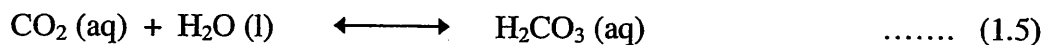


1.3 Solution Chemistry of Calcium Ion Dissolution

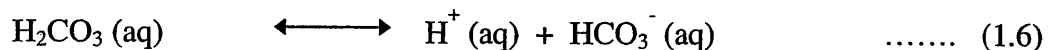
Rainwater generally contains carbon dioxide (CO_2) through absorption from the atmosphere:



The carbon dioxide dissolved in water can give rise to carbonic acid (H_2CO_3).

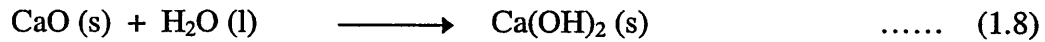


The carbonic acid ionizes significantly only so far as bicarbonate ion:



This in turn leads to an increase in the solubility of the calcium ions. In the presence of carbon dioxide, about 100 times as much calcium carbonate dissolves in water. (Normally 0.0143 g l^{-1} , as opposed to $0.94\text{-}1.08 \text{ g l}^{-1}$ in water containing dissolved carbon dioxide) [6]. The source of the calcium ions in the system under discussion will

be the portlandite, (4-6% in RPCC), the dolomite, the calcitic limestone, the calcium carbonate formed by carbonation of the portlandite, and calcium ions liberated from slag (calcium ions can also come from free lime [CaO]). However, the percentage of free lime in RPCC after thirty years of aging is probably minimal due to its interaction with water and carbon dioxide from the atmosphere. Previous research [1] showed that the free lime is generally considered to originate from the use of slag except ACBF slag as an aggregate material.



The rainwater permeating through the base or sub-base of the road becomes supersaturated with respect to the calcium ions and will have an increased pH. When the pH reverts back to neutral, a precipitation of calcium carbonate generally through nucleation from a suitable surface occurs. The change of pH is liable to occur when the leachate reaches the ceramic or concrete structure of the drainage “pots” at the side of the road.

The formation of calcite in the form of tufa is also going to be affected by other factors, such as the presence of ions other than calcium and some speculation on such factors as discussed earlier.

1.4 Objective of the Research Study

The following are the objectives set to study the magnitude of tufa precipitate problem present in the Recycled Portland Cement Concrete Aggregate:

1. To document the primary source of aggregate for the Portland cement concrete (PCC) pavement in the state of Ohio.
2. Characterisation of RPCC for tufa potential and establish the role of aggregates in RPCC for tufa forming potential.
3. To study the formation of $\text{Ca}(\text{OH})_2$ and CaCO_3 in the RPCC in the course of leaching by utilizing the Thermo gravimetric (TG) analysis process and Differential Thermal Analysis (DTA).
4. To study under controlled conditions the leaching of various ions, but especially Ca^{2+} from the RPCC. This can be achieved using atomic absorption spectrometry or associated techniques.
5. To develop a simple test to determine tufa potential of recycled Portland cement concrete aggregate.

1.5 The Present Study

The present research project involves the magnitude assessment of various elements that are present in the recycled Portland cement concrete aggregates. It requires a detailed study of the location of the RPCC aggregates and the type of the aggregates that went into the original manufacture of the concrete. It is then followed by detailed studies involving thermal analysis, X-ray powder diffraction (XRD), and leaching experiments involving acidic water - (water containing dissolved carbon dioxide). Examination of the leachate by the technique of Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The thermal analysis allowed the composition of the RPCC at each location to be established in terms of calcium carbonate, dolomite, and portlandite as well as indicating the presence of quartz. The XRD data showed the relative proportions of

calcium carbonate, dolomite, and quartz to be determined as well as indicating the presence of materials such as portlandite and gypsum, which would be expected to be present. The leachate experiments showed the amounts of calcium and magnesium ions, which dissolved in the presence of acidic water.

Chapter 2

Project Selection and Samples

2.1 Selection of projects for the study:

The Ohio Department of Transportation (ODOT) maintains Logbooks on Portland concrete pavement (PCC) pavement projects in the state of Ohio. The Logbooks contain information of PCC pavements for five different interstate highways in the state of Ohio. The five interstate PCC pavement highways for the sample study are I-70, I-71, I-75, I-77 and I-90. These pavements were documented in the Logbooks under a D-cracking study done by Portland Concrete Association (PCA), with the co-operation of Ohio Department of Transportation and the Federal Highway Administration (FHWA) and the US Department of Transportation. The Logbooks were made available to the research team for the selection of PCC pavements for the study. A matrix is prepared for all PCC pavement projects by considering variables such as: types and source of coarse and fine aggregates, source of cement, w/c ratio and meteorological conditions such as temperature, and their departures from the normal during the time of construction of pavements.

Portland Cement Concrete mix design consists of coarse aggregates, processed fine aggregates or natural sand, cement and water. The formation of tufa from cement depends on the amount of free lime available in cement. Cement consists of lime in combined form to impart strength to concrete. In general good quality cement does not produce tufa and good quality cement is used in the construction of pavements in Ohio. Natural sand used as fine aggregates to produce concrete will not produce tufa. On the other hand, if processed fine aggregates of dolomitic or calcitic origins are used to produce concrete, then it may be possible that the fine aggregates may produce tufa. Water cement (W/C) ratio plays an important role in the hydration process of concrete. An incomplete hydration may develop free lime that may be susceptible to produce tufa.

Generally coarse aggregates are gravel, lime, or slag aggregates used in construction of PCC pavements. Gravel aggregate consists of silica, whereas lime stone aggregates are rich in calcium carbonate and calcium oxide. Slag as coarse aggregates used in concrete may be either air cooled blast furnace (ACBF), open hearth (OH) or basic oxygen furnace (BOF). Earlier studies [1] have indicated that all slag except the ACBF slag will produce tufa. Thus, coarse aggregates type is included as one of the variables in the matrix to properly assess the formation of tufa. Meteorological conditions such as the temperature, precipitation, evaporation and wind during construction are very important to assess the completion of hydration process of the concrete. The meteorological conditions in terms of ambient temperature that may have effect on hydration is broadly divided into three temperature is incorporated in the matrix for the selection of RPCC aggregates samples.

2.2 Projects Selection Criterion:

Meteorological data was obtained from the Annual Weather Summaries of climatologic data for the state of Ohio, published by US Department of Commerce. Also some of the data was obtained from the State Climatology Office for the state of Ohio. Temperature ranges as below 50° F, 50-70° F, and over 70° F, are incorporated in the matrix for the selection of RPCC aggregates samples. The Maximum and Minimum ambient temperatures recorded during the month of construction period are also incorporated in the matrix to document extreme conditions the pavement was subjected. After preparing the matrix for all PCC pavements, initially 90 different projects of the RPCC aggregates were identified to characterise the tufa producing characteristics. Forty-seven projects out of the 90 projects were selected to receive PCC pavement core samples from the ODOT. Table 2.1 shows the number of projects selected for the study. Table 2.1 also shows selection of concrete pavement projects by aggregate types, meteorological condition and number of projects from each interstate state highway in the state of Ohio. These projects are selected from the D-cracking study logbooks.

TABLE 2.1

**SELECTION OF CONCRETE PAVEMENT PROJECTS FROM D-CRACKING STUDY LOG BOOKS BY
AGGREGATE TYPES AND METEOROLOGICAL CONDITIONS**

Concrete Pavement Projects on Interstate Highways	Gravel Aggregates			Limestone Aggregates			Slag Aggregates		
	Below 50°F	Between 50-70°F	Above 70°F	Below 50°F	Between 50-70°F	Above 70°F	Below 50°F	Between 50-70°F	Above 70°F
Pavement Survey Logbook I-70	3	2	2	2	1	2	3	2	0
Pavement Survey Logbook I-71	1	1	1	0	1	1	2	1	1
Pavement Survey Logbook I-75	2	0	2	1	1	1	0	0	0
Pavement Survey Logbook I-77	0	2	0	1	1	1	0	1	2
Pavement Survey Logbook I-90	0	0	0	1	1	1	0	1	2
Total Number of Projects = 47	6	5	5	5	5	6	5	5	5

2.3 Origin and Composition of the Samples

After discussion with the ODOT personnel, some of the projects were dropped to receive samples. Table 2.2 lists the projects for which the ODOT has provided cores of PCC pavements. It should be noted that the ODOT was unable to supply samples for project sample ID # I75-#1, 2 and 4 due to heavy traffic condition. The Table 2.2 shows the samples identification number, county name, mile marker, project number, mix design, source of fine aggregate and cement, ambient temperature during construction, precipitation and date paved. It should be noted that the latest date for date paved is 1968, so these samples had been subjected to over 30 years of weathering. The Table 2.2 also shows the maximum temperature recorded in the month of pavement was constructed. The Table 2.2 is formatted in five different sections A through E to distinguished projects for each interstate highway. Information such as supplier of fine aggregates, name of the paving company for each selected project are included in Table A.1 in the Appendix A. The Table A.1 also shows the concrete pavement project by mile marker for each interstate highway and the corresponding designated number used in the current research project for the identification of sample numbers.

2.4 Preparation of Samples

Samples received from the ODOT were 6 inches diameter core of the entire thickness of PCC pavement. Some pavement cores had asphalt overlay, thus in a laboratory asphalt was separated from PCC for preparation of samples. The PCC core samples were crushed using a Universal Testing Machine (UTM) and then in a "Chip Munk" crusher to obtain coarse and fine aggregates. Here in called recycled Portland cement concrete (RPCC) aggregates. In the first stage of sieving, the aggregates collected were separated into two categories: (i) coarse aggregate and (ii) fine aggregate. These aggregates were stored in plastic bags and properly labelled for the leachate experiments.

Furthermore, the leachate experiments require nominal size of coarse aggregates so a narrow particle size distribution of the coarse aggregate was developed. The

Table 2.2

**PCC PROJECTS BY COUNTY NAME, MILE MARKER, MIX DESIGN, TEMPERATURE,
PRECIPITATION AND PAVING DATE**

Section A). Projects Selected from I – 70

Sample #	Mix design										Paved Date
	Course Aggregate			Fine Aggregate	Cement	Temp <50°F (Dep)	Temp 50 – 70°F (Dep) ²	Temp > 70°F (Dep)	Max Temp (min)	Precipitation In inches (Dev) ³	
	Gravel	Lime	Slag								
I-70#1	# 3Gr - Am Aggregate			Am Aggregate	Universal		62 (0.2)	3.49 (0.63)	61 (34)	3.49 (0.63)	Nov 61
I-70#2	# 3Gr - Am Aggregate			Am Aggregate	Huron			2.97 (0.96)	87 (54)	2.97 (0.96)	July 64
I-70#3	# 3Gr - Am Aggregate			Am Aggregate	Universal	49.8 (-3.1)		0.38 (1.73)	68 (40)	0.38 (1.73)	Oct 63
I-70#4		# 3 Limestone		Steiner	Universal		69.6 (3.1)	.07 (-0.06)	80 (55)	.07 (-0.06)	Sep 59
I-70#5	# 3 & 4 Gr Aggregate			Feuton Constr Co Fine	Universal & Miami		66.4 (-0.1)	2.99 (0.08)	86 (41)	2.99 (0.08)	Sep 57
I-70#6	# 3Gr - Am Aggregate			Feuton Constr Co Fine	Alternate Universal / Miami	43.4 (1.5)		3.23 (0.37)	64 (30)	3.23 (0.37)	Nov 57
I-70#7	# 3Gr - Am Aggregate			Feuton Constr Co Fine	Universal			0.89 (-2.32)	83 (54)	0.89 (-2.32)	Aug 57

I-70#8		# 3 Limestone Marble		Am Aggregate	Columbia	45.1 (3.9)			65 (36)	1.81 (-0.69)	Nov 64
I-70#9		# 3 Limestone Marble		Am Aggregate	Columbia			72 (-2.8)	86 (64)	4.76 (1.76)	July, Aug 65
I-70#10		-# 3 Limestone Marble		Am Aggregate	Dundee	45.1 (3.9)			65 (36)	1.81 (-0.69)	Oct, Nov 64
I-70#11		# 3 Limestone Marble		Am Aggregate	Dundee			71.4 (0.6)	83 (57)	1.28 (-2.88)	June 66
I-70#12		#57 Limestone Aggregate		Fine River Gravel	Columbia			71.3 (-1.9)	80 (67)	4.90 (2.04)	Aug 66
I-70#13	# 3Gr - Am Aggregate			Fine Gravel	Huron	45.9 (3.9)			65 (36)	1.81 (-0.69)	Nov 64
I-70#14			# 57 Slag	Fine Sand	Diamond		68.3 (0.0)		80 (59)	6.18 (3.53)	Sep 65
I-70#15			# 57 Slag	Fine Sand	Diamond		63.2 (-2.7)		78 (57)	3.56 (0.91)	Sep 66
I-70#16			# 57 Slag	Fine Sand & Gravel	Unknown	49.8 (-3.1)			68 (48)	0.38 (-1.73)	Oct 64
I-70#17			# 3 Slag	Fine Sand & Gravel	Diamond	49.8 (-3.1)			68 (48)	0.38 (-1.73)	Oct 64

The Results are obtained from PAVEMENT SURVEY LOG FOR I - 70 and METEOROLOGICAL data by US DEPARTMENT of COMMERCE .

Section B). Projects Selected from I – 71

Serial #	Mix design				Temp <50°F	Temp 50–70°F	Temp >70°F	Precipitation (Dep)	Paved Date	
	Course Aggregate			Fine Aggregate						Cement
	Gravel	Lime	Slag							
I-71#1	# 3Gr Aggregate			Queens City Gravel	Miami	49.8 (-2.9)		1.49 (-1.03)	Oct 66	
I-71#2	# 3Gr Aggregate			Ohio Fine Aggregate	Kosmos		55.6 (4.3)	2.9 (-1.08)	May 66	
I-71#3	# 3Gr Aggregate			Ohio Fine Aggregate	Dundee			76.8 (0.4)	3.17 (-0.5)	In July 64
I-71#4		#3 limestone		Ohio Gravel	Miami		53.8 (-2.7)	0.66 (-1.22)	In Oct 63	
I-71#5		#3 limestone		Ohio Gravel	Miami, Universal			72.9 (0.2)	5.55 (1.76)	In June 64
I-71#6			# 3 Cleveland Slag	Fine Sand & Gravel			67.6 (-0.3)	1.76 (-0.56)	Paved Sep 64	
I-71#7			# 3 Cleveland Slag	Fine Sand & Gravel	Columbia			74.3 (-0.3)	3.44 (0.23)	Paved July 65
I-71#8			# 57 Cleveland Slag	Fine Sand & Gravel	Bessemer	49.8 (-2.9)		1.49 (-1.03)	In Oct 66	
I-71#9			# 57 Cleveland Slag	Fine Sand & Gravel	Huron & Dundee	34 (3.0)		3.35 (-0.43)	In Nov, Dec 67	

The Results are obtained from PAVEMENT SURVEY LOG FOR I – 71 and CLIMATOLOGY Data by U.S DEPARTMENT OF COMMERCE .

Section C). Projects Selected from I – 75

Serial #	Mix design										Paved Date
	Course Aggregate			Fine Aggregate	Cement	Temp <50°F (Dep)	Temp 50-70°F (Dep)	Temp >70°F (Dep)	Max Temp (Min)	Precipitation (Dep)	
	Gravel	Lime	Slag								
I-75#1	# 3Gr Ohio Aggregate			Ohio Fine Gr Aggregate	Universal & Miami	40.2 (-1.8)			63 (30)	2.85 (-0.62)	In Oct, Dec 62
I-75#2	# 3Gr Aggregate			Ohio Fine Gr Aggregate	Universal			70.1 (0.6)	79 (64)	4.47 (-1.11)	In Aug 58
I-75#3	# 3Gr Ohio Aggregate			Ohio Fine Aggregate	Peninsular	38.4 (-3.6)			58 (36)	3.37 (0.24)	In Nov 59
I-75#4	# 3Gr - Am Aggregate			Am Aggregate	Universal			70.5 (-2.0)	87 (68)	3.06 (-1.02)	Paved July 65
I-75#5		# 3 Limestone		Fine Sand & Gravel	Universal, Medusa, Huron			75.4 (4.7)	81 (66)	2.45 (-1.13)	Paved Aug 59
I-75#6		#3 Limestone		Fine Sand & Gravel	Medina	49.8 (-2.9)			60 (47)	1.49 (-0.97)	Paved Oct 66
I-75#7		#3 Limestone		Fine Sand & Gravel	Miami		57.1 (4.4)		76 (41)	2.77 (-1.41)	Paved July 57

The Results Are Obtained From PAVEMENT SURVEY LOG FOR I – 75 And CLIMATOLOGICAL DATA By US DEPARTMENT OF COMMERCE .

Section D). Projects Selected from I – 77

Serial #	Mix design				Cement	Temp <50°F (Dep)	Temp 50-70°F (Dep)	Temp >70°F (Dep)	Max Temp (Min)	Precipitation (Dep)	Paved Date
	Course Aggregate			Fine Aggregate							
	Gravel	Lime	Slag								
I-77#1		# 57 Limestone		Fine River Sand &Gravel	Columbia			72.3 (-0.2)	80 (65)	3.52 (-0.56)	In July 68
I-77#2	# 57 Gr Aggregate			Fine Sand &Gravel Aggregate	Diamond		61.6 (-2.6)		78 (57)	3.02 (-0.1)	In Sep 66
I-77#3	# 3Gr Aggregate			Fine Sand &Gravel Aggregate	Columbia		58 (0.1)		70 (43)	4.35 (0.37)	In May 60
I-77#4		# 3 Natural Lime		Fine Sand &Gravel Aggregate	Columbia		61.3 (-2.9)		77 (50)	3.81 (0.69)	In Sep 62
I-77#5			# 57 Slag Aggregate	Fine Sand &Gravel Aggregate	Dundee		54.2 (1.5)		71 (46)	1.96 (-0.56)	In Oct 68
I-77#6			# 57 Slag Aggregate	Fine Sand &Gravel Aggregate	Bessemer			72.4 (1.7)	80 (66)	3.54 (-0.04)	In Aug 68
I-77#7			# 3 Slag Aggregate	Fine Sand &Gravel Aggregate	Standard			72.7 (0.2)	81 (66)	3.52 (-0.56)	In July 58
I-77#8		# 3 Limestone		Fine Sand &Gravel Aggregate	Bessemer	42.8 (0.8)			59 (37)	2.01 (-1.12)	In Nov 65

The results are obtained from the PAVEMENT SURVEY LOG FOR I-77 and CLIMATOLOGICAL DATA by US DEPARTMENT of COMMERCE.

Section E). Projects Selected from I – 90

Serial #	Mix design					Temp <50°F (Dep)	Temp 50-70°F (Dep)	Temp >70°F (Dep)	Max Temp (Min)	Precipitation (Dep)	Paved Date
	Course Aggregate			Fine Aggregate	Cement						
	Gravel	Lime	Slag								
I-90#1			#4 & 6 Slag and US Steel	Fine Sand & Gravel	Medusa			70.4 (-2.1)	79 (64)	3.62 (-0.46)	In July 67
I-90#2		# 57 Limestone Aggregate		OhioFine Sand & Gravel	Peerless			72.3 (-0.2)	80 (65)	3.52 (-0.56)	In July 68
I-90#3		# 57 Limestone Aggregate		Natural Sand & Gravel	Bessemer		56.7 (-3.3)		65 (52)	7.71 (3.73)	In May 68
I-90#4		# 57 Limestone Aggregate		Natural Sand & Gravel	Bessemer	34.0 (3.0)			50 (36)	5.44 (2.53)	In Dec 67
I-90#5			#3 Slag Cleveland	Natural Sand & Gravel	Standard		53.5 (0.8)		70 (41)	1.89 (-1.63)	In Oct 60
I-90#6			#3 Slag Cleveland	Natural Sand & Gravel	Standard			71.0 (-1.5)	87 (61)	4.47 (-0.39)	In July 62

The Results are obtained from PAVEMENT SURVEY LOG FOR I – 90 and METEOROLOGICAL data by US DEPARTMENT of COMMERCE .

1. Mile Marker from County Line.
2. Departure from the Normal Temperature.
3. Deviation from the Normal Precipitation.

aggregates that passed through the opening of 1/2" and retained on 3/8" was collected for coarse aggregate leaching test.

In a second stage of sieving, particles passing through ASTM sieve # 230 and retained on ASTM sieve # 325 were processed in polypropylene bottles for the Ethylene Glycol test. The Particles passing through sieve # 200 were stored in glass vials for the TG-DTA and XRD experiments.

2.5 Additional Samples

In a process to establish a base line to measure the magnitude of Ca^{2+} in the Portland cement concrete pavement samples, the ODOT has supplied additional five samples as shown in Table 2.3. One sample is from the I-75 reconstruction project near Perrysburg, Ohio. This sample is virgin 304 aggregates used for base and subbase coarse. Other four samples are rubblized concrete in chunks. Two samples each are from Medina and Greene County respectively. It is hoped that experimental results from these samples will provide a base line for comparison of experimental results from RPCC samples. Table 2.3 shows the sample identification number, location and type of aggregates.

Table 2.3

RPCC and 304 Aggregate Samples by locations and Types of Aggregates.

Sample #	Location of Sample	Type of Aggregate
RC-1	MED-271#1	Gravel
RC-2	MED-271#2	Gravel
RC-3	GRE-35J#1	Cobble and Gravel
RC-4	GRE-35J#2	Gravel
304 (Fine Aggregate)	Lucas	Limestone
304 (Coarse Aggregate)	Lucas	Limestone

Chapter 3

Literature Review

3.1 Calcite Precipitation model

Bruinsma etc. [5] suggested a simple model for calcite precipitation in RPCC aggregates. They showed that carbon dioxide plays an important role in precipitation of calcite in limestone caverns, as well as in the precipitation of calcite in RPCC aggregates. Gupta and Kneller in their studies [1] showed that the in-availability of CO_2 in the base layer becomes a primary issue in the dissolution. Pore waters in the base layer are isolated from atmosphere CO_2 by the overlaying pavement structure. Portlandite within RPCC aggregates base layers dissolves readily when exposed to water, yielding high concentrations of Ca^{2+} and OH^- ions that is demonstrated by the high pH values. Although an abundance of Ca^{2+} ions are available in pore water solution, but without a major source of CO_3^{2-} , the formation of calcite is limited.

To understand the magnitude of free and hydrated lime present in the RPCC aggregates, a study of equilibrium and rates of reaction (chemical kinetics) is essential. There are numerous studies of chemical kinetics underway to develop a better understanding of reactivity rates. The important factors that influence reaction rates are temperature, size, shape and electric charge of the reaction solute species ionic strength of the solution, viscosity and pressure [7].

Dissolution and precipitation rates of solid phases may be controlled by three types of mechanism (a) reaction at the surface (boundary) of the mineral, (b) transport of molecules or ions in solution to or from the mineral surface, and (c) diffusion of molecules or ions through a layer of solid reaction products (or a

layer of partially altered primary mineral surrounding the solid) [8]. Some reactions are diffusion (or transport) controlled, while others are chemically controlled [7]. Chemically controlled process may take one step or be more complex, consisting of a number of steps that create the overall reaction mechanism [7]. Chemical transformation can include the formation of an activated complex (i.e., intermediate reactant) or a set of reactions taking place in series or parallel, each possibly being reversible or irreversible. In a dissolution/precipitation mechanism, several reaction under the saturation and affinity environment may take place.

Shiraki etc. [9] showed that the important factor in the kinetic chemistry of RPCC precipitation is contact time between carbonic acid rich water and RPCC aggregates. Contact time is dependent on the resident time of drainage waters (i.e., the ability of a base layer to drain water). In open graded bases there is a shorter residence time, thus providing a smaller dissolution leading to small calcite precipitation. Gupta and Kneller [1] in their previous research study showed that the particle size of aggregates effects the precipitation. A higher percentage of fine RPCC aggregates will have a larger amount of surface area that will lead to increase in calcite precipitation.

3.2 The Carbonic Acid System

Strength of carbonic acid is measured by its dissociation constant which is commonly reported by analogy with pH. Chemically it has been shown that the lower pH will have higher dissociation and hence stronger the acid. In the chapter 1 it has been stated that the rainwater rich in carbonic acid leads to the dissolution of Ca^{2+} ions. Another property of carbonic acids (or, more importantly, the corresponding anions) is the ability to combine with complex metals, especially transition metals and aluminium. A third property of carbonic acid is its effect on solubility and related properties. An ionised carbonic acid greatly increases the

solubility in water of the compound to which it is attached. This is important in the adsorption properties of the compound and specially in the dissolution of Ca^{2+} ions.

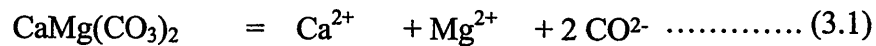
Generally when gas CO_2 is brought into contact with water, the CO_2 will dissolve until equilibrium is reached. At equilibrium, the concentration of dissolved carbon dioxide will be proportional to the pressure of CO_2 in the gas phase. In the natural environment, the normal convention is to refer all dissolved carbon dioxide as H_2CO_3 . The H_2CO_3 is responsible for the dissolution Ca^{2+} ions and production of tufa. A measure of pH of rainwater and surface water close to highways will provide an accountability of dissolution Ca^{2+} ions and production of tufa. Drever [8] conclude in his book that at pH values close to 6.4 the dissolved carbonate species are in the form of H_2CO_3 and above pH 7 essentially all are in the form of HCO_3^- .

3.3 Calcium Carbonate Solubility

Garrels and Christ [10] provide the calcite solubility at various temperatures. At 25°C the solubility of calcite is $10^{-8.35}$. In most surface waters saturated with calcite have pH values between 7.3 and 8.4. Aggregates containing both Ca and Mg ions will have different solubility for their carbonate forms. Calcium carbonate has a solubility of 3.8×10^{-9} and magnesium carbonate has 3.5×10^{-8} which indicates that magnesium carbonate has higher solubility as compared to calcium carbonate. Thus, in case of both ions present in solution will create a common ion effect (the common ion in this case is carbonate). Because of different solubility of calcium and magnesium, magnesium will remain in solution and calcium will combine with carbonate to form calcium carbonate to precipitate as tufa.

3.4 Dolomite

Dolomite has a chemical formula $\text{CaMg}(\text{CO}_3)_2$, and a crystallographic structure similar to that of calcite, except that the Ca and Mg atoms are arranged in separate planes. The ordering of Ca and Mg atoms distinguishes dolomite from a high magnesium calcite of the same composition. The solubility of dolomite can be represented by the equation:



There has been considerable disagreement in the literature as to the correct value of $\text{CaMg}(\text{CO}_3)_2$. The disagreement results from the fact that the dolomite is very un-reactive at low temperatures and dolomite dissolves only slowly in solutions that are strongly under saturated with respect to it.

In nature, dolomite is generally formed by alteration of calcite or aragonite:



A ratio of Mg/ Ca provides some insight of association and dissociation of calcite and magnesium in solution. The solution in which the ratio of Mg/ Ca is higher than 0.60, the dolomite is more stable than calcite and vice versa.

Although there is a large uncertainty associated with this number, but calcite is probably unstable with respect to dolomite in surface waters in which the Mg/Ca ratio is higher than 1 [11]. In higher Mg/Ca ratio, the calcite is unstable and may combine with CO_2 to form CaCO_3 .

In general, the Ca – Mg carbonate solid solution will be highly non- ideal, so no simple linear relationship exist between the concentration ratio in the solid and the concentration ratio in solution [8]. However, for any particular ratio in solution, there is a corresponding unique ratio in the solid, and when the ratio in solution varies, so should the ratio in the solid. Generally solubility equilibrium

is more strictly defined by the stoichiometric saturation. Measurement of solubility is complicated by the fact that when high magnesium calcites are placed in water, they initially dissolve congruently, but as the concentration of ions in solution increases, dissolution becomes incongruent.

During incongruent dissolution, a low-magnesium calcite precipitates as the high-magnesium calcite dissolves [8]. Plummer and McKenzie [12] and Bischoff et al. [13] estimated the solubility of high-magnesium calcites by measuring the rate of dissolution when dissolution was constant and extrapolating the results to finite time. This approach was criticized by Lafon [14] and by Garrels and Wollast [15], but there is a consensus that calcites containing some magnesium, probably up to 5 mole percent $MgCO_3$, are more stable than pure calcite.

3.5 Precipitation and Equilibrium Chemistry

In general rainwater is in equilibrium with atmospheric carbon dioxide, which has a partial pressure of $10^{-3.35}$ atm. As rain percolates through pavement and moves through aggregates, if additional CO_2 is not available than the system is closed and the amount of $CaCO_3$ dissolved will be limited. If system is open to CO_2 , than CO_2 will be transferred from gas phase to replace the CO_2 consumed by dissolution of calcite. In this case, the dissolution of calcite is higher than under closed system condition. This leads to a conclusion that to control the dissolution of calcite the system should be a closed one. Under the normal condition it can be concluded that in a rock containing both calcite and dolomite, the water ultimate come to equilibrium with calcite and dolomite. Thus a ratio of dissolve Mg/ Ca of 0.6 provides a guidelines in the precipitation chemistry [16].

Chapter 4

Laboratory Studies of RPCC Samples

4.1 Thermal Analysis

Thermal analysis is the study of chemical and physical changes in a given material due to changes in temperatures. These temperature changes are usually linear with time. The changes in enthalpy, which accompany chemical and physical changes, can be observed and recorded. These enthalpy changes, either exothermic (+) or endothermic (-) are caused by phase transitions such as fusion, crystalline structural inversions, boiling, sublimation, and vaporization; dehydration reactions; dissociation reaction or decomposition reactions; oxidation and reduction reactions; destruction of crystalline structures; and other chemical reactions. Generally, phase transitions, dehydration, reduction and some decompositions produce exothermic effects.

There are five basic categories or techniques of thermal analysis: thermometry, differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermo mechanical analysis and dilatometry (TMA), and thermogravimetry (TG). The technique used in this study is thermogravimetry.

4.2 Thermogravimetry

Thermogravimetry analysis (TGA) measures the loss of weight by a substance as the temperature of the substance is raised or lowered at a constant rate. The reactions that occur during the heating process are responsible for the changes in weight. Knowing that certain reactions occur at specific temperatures enables the identification of the constituents of the sample. Generally two types of TGA are usually conducted on the cement and limestone samples. The first method is thermo gravimetric analysis (TGA). This works by placing a crucible on a microbalance and setting the weight to zero. The crucible is then filled with a sample and the weight is recorded by the equipment. The sample and microbalance are then put into a furnace that produces a linear heating rate.

As the sample is heated, chemical reactions take place. As the reaction takes place, any weight change is recorded by the microbalance. The TGA records temperature and weight simultaneously. The temperature is measured by a thermocouple that is usually located below the crucible [17]. An example of a weight gain would be an oxidation reaction. An example of a weight loss would be a decomposition reaction, such as calcium carbonate going to calcium oxide and carbon dioxide, which is lost to the atmosphere. The furnace atmosphere is also important; if the atmosphere is nitrogen, no oxidation reactions can take place [17]. The furnace atmosphere is controlled by hooking up a compressed gas cylinder and passing gas at a rate of 100 ml per minute. The temperature versus percentage weight loss is then plotted.

The second type of thermoanalysis used is differential thermal analysis (DTA). This is similar to the TGA, but two cells are used. The sample is in one crucible and a reference material is in the second crucible [17]. The reference material used for the analysis in this study was an empty crucible that would always be at the furnace temperature. The DTA records both of the cell temperatures and measures the difference in the temperatures. If the sample temperature is lower than the reference temperature an endothermic reaction is taking place [17]. This is useful for measuring reactions in which a weight change does not take place, such as melting, or a change in crystal structure, such as aragonite changing to calcite. The temperature versus difference in temperature is then plotted. The physicochemical applications of thermogravimetry are listed in Table 4.1 [18]. The Table 4.1 lists the physical and chemical changes in the sample material through the applications of thermogravimetry. It shows that various state of physical and chemical changes that may occur to the sample under TGA test. It should be noted that in nature, free lime does go through physical and chemical changes to precipitate as tufa. Table 4.1 shows changes in terms of $\text{solid}_1 + \text{gas} \rightarrow \text{solid}_2$ or $\text{solid}_1 \rightarrow \text{solid}_2 + \text{gas}$ in conformity to the discussion of Chapter 1.

Table 4.1

Physicochemical Applications of Thermogravimetry

Physical Changes
Sublimation
Vaporization
Absorption
Adsorption
Magnetic Properties: 1. Curie Temperature 2. Magnetic Susceptibility

Chemical Changes (Solid → Gas)
Gas
Thermal Decomposition of many organic and polymeric substances
Pyrolysis of coal, petroleum and wood.
Thermal oxidation, degradation of polymeric materials.
Carbon gasification with oxygen, steam, or carbon monoxide.

Chemical Changes (Solid₁ + Solid₂ → Solid₃ + Gas)
Dehydration studies
Determination of moisture, volatiles, and ash contents.
Development of analytical procedures
Kinetic Studies (Also applicable to solid-gas).
Thermal decomposition of many organic material.
Dehydroxylation Studies
Roasting and calcining of minerals.
Decomposition of explosives

Chemical Changes (Solid₁ + Gas → Solid₂).

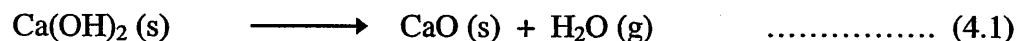
Chemical Changes (Solid₁ → Solid₂ + Gas).

Reference: [8].

4.3 Thermal Analysis Experiment

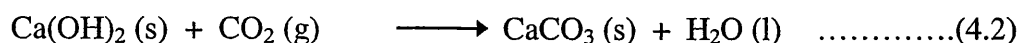
In the research study, thermal analysis experiments were conducted on each of the RPCC samples supplied by the ODOT. In a laboratory study temperature changes are regulated to produce a linear response with time. Thermal analysis experiment measures changes in chemical and physical properties of a given material as the temperature is changed under a controlled condition. Temperature changes are usually regulated to give a linear response with time. Thus a heating rate of 10°C per minute was employed in the present study. The TG instrument actually used in the present study was a simultaneous unit measuring changes in temperature (Differential Thermal Analysis, DTA) at the same time as noting the changes in mass (Thermogravimetry, TG) both as a function of time or temperature.

RPCC aggregates normally contain cement and fine and/or coarse aggregates. The hydration of the cement will cause the formation of portlandite (see equations 1.1 and 1.2). At around 400°C the RPCC aggregates will undergo decomposition according to the following equation:

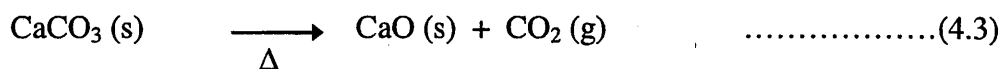


It was observed that in nitrogen atmosphere, around 0.6 to 1.0 percent mass loss at the temperature range of 402 to 460°C was detected.

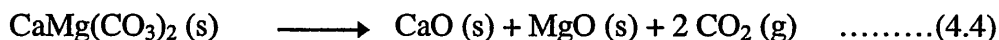
Due to the aging of present RPCC samples over thirty years, the portlandite, would have undergone considerable carbonation with atmospheric carbon dioxide as shown below:



The calcium carbonate in the sample (as shown in equation 4.2) upon heating, will decomposed to calcium oxide as given below:



In nitrogen atmosphere, the dolomite [$\text{CaMg}(\text{CO}_3)_2$] will decompose in a single stage:



The mass loss is approximately 30 to 40% at the temperature of 460 to 800°C. However, in carbon dioxide atmosphere, the decomposition of the dolomite occurs in two stages:



The first stage mass loss is around 4 to 16% at the temperature of 500 to 800°C. Then, the residual carbonate (CaCO_3) will decompose according to equation 4.3. The temperature of decomposition of calcium carbonate under these conditions (i.e. one atmosphere of carbon dioxide) will be slightly higher than in nitrogen.

4.3.1 TG-DTA Results and Analysis

All the above events are recognised in the thermal analysis experiment of RPCC. A typical TG-DTA result for I-70#1 sample under CO_2 atmosphere at a heating rate of $10^\circ \text{C min}^{-1}$ is shown in Figure 4.1. It can be seen that in the atmosphere of carbon dioxide the dehydroxylation of the portlandite, the first stage of the decomposition of dolomite, and the decomposition of calcium carbonate occurs at temperature 780°C . The amount of portlandite in these aged samples of concrete is diminished over the normal

Sample: I70 # 1
Method: 10°C/MIN TO 1100°C
Comment: Dry CO2, 100 mL/min

TGA-DTA

File: C:\ODOT\I70-1.c01
Operator: Supaporn

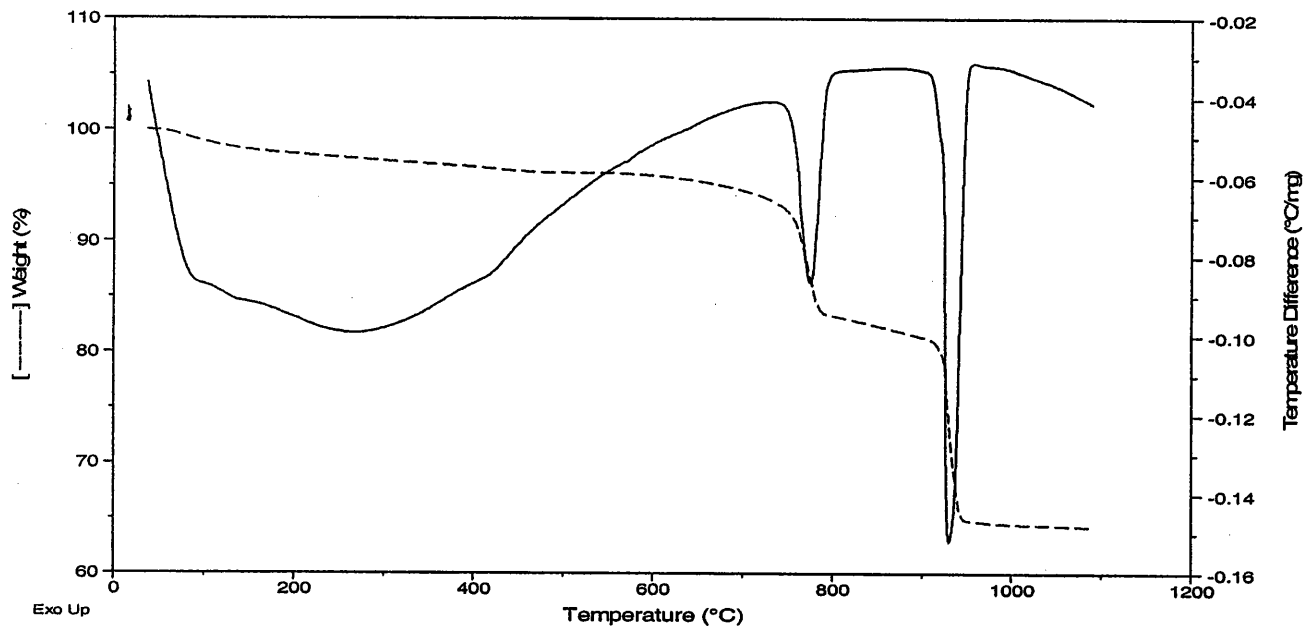


Figure 4.1 Typical TG-DTA Plots for RPCC Aggregate Sample I-70#1 Tested under a CO2 Atmosphere, at a Heating Rate of 10⁰ C min⁻¹.

expectations for concrete because of the carbonation from the air. The dolomite content of the concrete can be measured from the initial peak (first stage) for the dolomite decomposition. The subsequent decomposition of the calcium carbonate (second stage) occurs at 950⁰ C and originated from: (i) calcite, originally present as the aggregate, (ii) the carbonation of portlandite, and (iii) the prior decomposition of dolomite.

The methods of calculation are given in Appendix B, together with the TG-DTA plots for all the RPCC aggregates examined. It is possible to present this data as the differential plots (DTG) under CO₂ atmosphere at a heating rate of 10° C min⁻¹ and this is shown in Figure. 4.2 as an example. The DTG plot clearly shows the first stage weight loss at temperature 800°C and the second stage weight loss at temperature 950°C. Beyond these two weight loss, there is no further weight loss indicating that the decomposition of CaCO₃ is complete.

The TG-DTA experiments are repeated under N₂ atmosphere at the same heating rate of 10° C min⁻¹. Figure 4.3 shows a typical plot for the same sample I-70#1. A comparison of Figures 4.1 and 4.3 show that there is a higher decomposition of CaCO₃ in N₂ atmosphere.

Table 4.2 lists the results of the calculations based on the thermal analysis experiments tested in the carbon dioxide atmosphere. The Table shows the variation of percentage of calcite across the sample. It varies from a low of 0.26 percent to a high of 47.80 percent. Because of wide range of variation of calcite no definite conclusion could be drawn. It only suggests that sample has a presence of calcite. Only two samples I-77#8 and I-90 # 1 have negligible presence of calcite. The DTA signal can be used to indicate the presence of quartz. This is determined by a reversible transition shown at around 573°C [19,20]. In the CO₂ atmosphere at 8000 temperature, the percentage weight loss is 15 percent as compared to a 35 percent weight loss in N₂ atmosphere. A further analysis of Table 4.2 by aggregate types suggests that percentage of calcite is higher in

Sample: I70 # 1
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-1.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

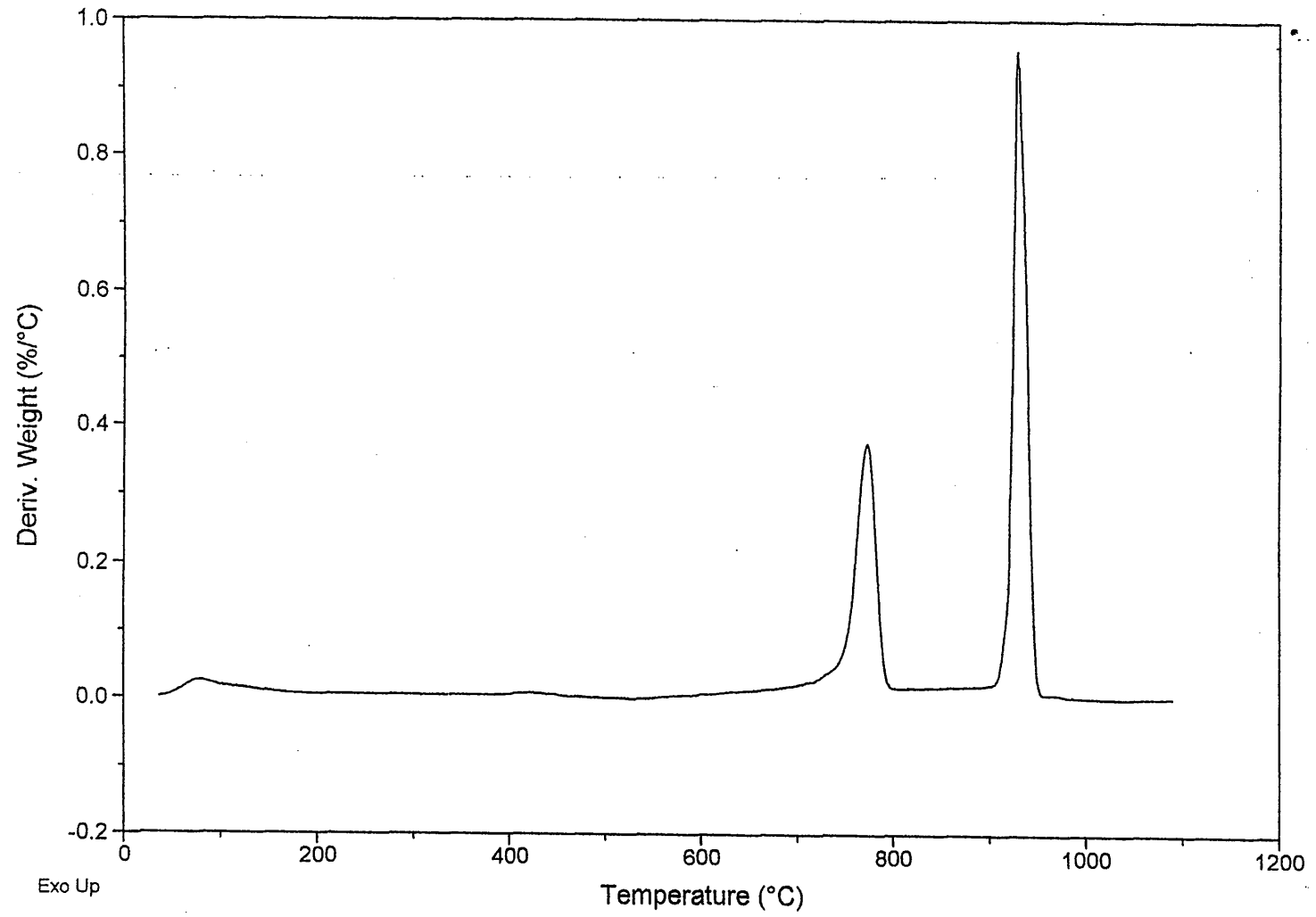


Figure 4.2 Typical DTG Plot for RPCC Aggregate Sample I-70#1 tested under a CO₂ Atmosphere, at a Heating Rate of 10°C min⁻¹

Sample: I-70 # 1
Method: 10°C/MIN TO 1000°C
Comment: Dry N2, 100 mL/min

TGA-DTA

File: C:\ODOT\I70-1.n01
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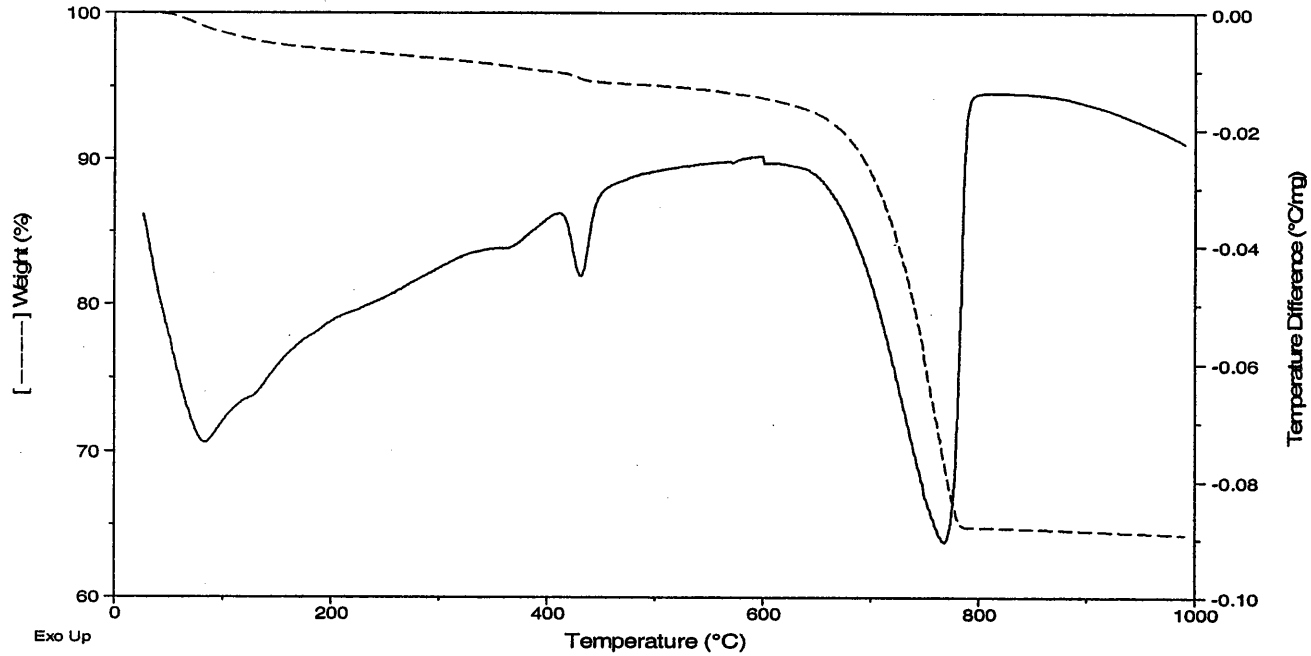


Figure 4.3 Typical TG-DTA Plots for RPCC Aggregates Tested under a N₂ Atmosphere, at a Heating Rate of 10⁰ C min⁻¹

Table 4.2

Thermal Analysis Experimental Results for RPCC samples in CO₂ Atmosphere.

Sample#	Type of Coarse Aggregate	% Portlandite (TG Data)	% Dolomite (TG Data)	% CaCO₃ (TG Data)
I-70#1	Gravel	2.92	55.18	12.46
I-70#2	Gravel	4.27	69.12	5.41
I-70#3	Gravel	3.41	29.77	16.87
I-70#4	Limestone	3.62	47.2	18.51
I-70#5	Gravel	2.84	61.01	9.45
I-70#6	Gravel	3.70	62.86	8.24
I-70#7	Gravel	3.82	57.48	0.26
I-70#8	Limestone	3.82	44.93	20.99
I-70#9	Limestone	3.12	51.14	23.07
I-70#10	Limestone	3.78	49.93	14.51
I-70#11	Limestone	3.95	7.73	5.5
I-70#12	Gravel	3.00	16.96	6.86
I-70#13	Slag	2.88	21.75	2.93
I-70#14	Slag	2.67	13.56	5.35
I-70#15	Slag	3.62	16.17	0.26
I-70#16	Slag	4.56	65.21	2.47
I-70#17	Slag	3.21	17.05	5.05
I-71#1	Gravel	2.84	40.69	25.84
I-71#2	Gravel	2.42	15.58	43.19
I-71#3	Gravel	2.71	47.16	21.62
I-71#4	Limestone	3.86	75.16	3.58
I-71#5	Limestone	3.41	65.63	7.97
I-71#6	Slag	3.00	11.67	2.02

I-71#7	Slag	2.01	20.41	41.72
I-71#8	Slag	2.84	13.35	47.80
I-71#9	Slag	2.71	17.89	30.06
I-75#1	Gravel	-	-	-
I-75#2	Gravel	-	-	-
I-75#3	Gravel	3.82	65.80	8.03
I-75#4	Gravel	-	-	-
I-75#5	Limestone	4.40	69.12	2.89
I-75#6	Limestone	3.58	65.00	7.85
I-75#7	Limestone	5.06	66.55	3.76
I-77#1	Limestone	2.84	30.07	16.30
I-77#2	Gravel	3.04	14.19	8.32
I-77#3	Gravel	2.84	36.70	5.55
I-77#4	Limestone	4.07	50.93	17.39
I-77#5	Slag	2.22	12.56	2.67
I-77#6	Slag	3.16	13.48	0.58
I-77#7	Slag	1.69	60.00	0.57
I-77#8	Limestone	4.15	15.31	0
I-90#1	Slag	2.01	67.06	0
I-90#2	Limestone	3.33	33.55	22.65
I-90#3	Limestone	3.16	20.62	9.08
I-90#4	Limestone	2.67	13.31	2.97
I-90#5	Slag	2.06	11.76	6.90
I-90#6	Slag	3.62	57.74	1.08

* : Notation Used in the Table:

C- Calcite, D-Dolomite, Q-Quartz.

1. QT -Quartz Transition.

2. NQT - No Quartz Transition.

3. -- Not Available.

limestone aggregate as compared to gravel. Most of the samples of slag aggregates show a small percentage of calcite except three samples.

4.4 X-ray Powder Diffraction

The X-ray powder diffraction method (XRD) relies on a quantity of powdered material being irradiated by a beam of monochromatic X-rays. The quantity of material presented in this manner is such that their random orientation also results in all lattice planes being favourably presented to the beam. The X-ray beam will strike a particular set of parallel layers of atoms in the crystal at an angle designate as θ (theta). The rays colliding with the atoms in the first layer will be reflected at the same θ . Those rays colliding with the second layer, third layer and so on will also be reflected at the angle θ . A reflected beam results only if all rays are in phase.

In order for the waves to be in phase, the difference in path length must be equal to the wavelength (λ) times an integer n. This leads to the condition represented by the Bragg equation:

$$n \lambda = 2d \sin \theta \dots\dots\dots(4.6)$$

where d is the distance between adjacent lattice planes of constituent atoms in the crystal, and θ is the glancing angle of incidence of the X-ray to the surface of the crystal. The data collected is plotted as the intensity of the reflected X-ray against the angle (usually designated as 2θ). Once the XRD patterns of the samples are collected, such patterns are compared with standard XRD patterns provided by the Joint Committee for Powder Diffraction Standards (JCPDS). From the agreement between the sample and the JCPDS patterns, the components under study could be identified [21,22].

The use of an X-ray powder diffraction instrument in this way produces an X-ray diffraction pattern, which can be used for mineral identification purposes. Although the

method can be used quantitatively, it is used here simply to identify mineral components present and to assess their relative abundance.

4.4.1 XRD Equipment

A Scintag XDS2000, X-ray Powder Diffractometer, was employed in this research study. The data were processed using DMS2000 (version 2.0) software on Microvax 3100 with Tektronix 4207 for graphical display. The X-ray was produced by Cu at a wavelength of 1.5406Å (CuK α) and detected by a solid state Ge detector cooled by liquid nitrogen. The K α_2 data have been stripped from the raw intensity, and the background was subtracted using “fast fourier filtering”. The experimental conditions were as follows: a voltage at 45 kV and a current at 40 mA, divergent beam slits of 2 and 4 mm, receiving slits of 1 and 0.2 mm, 2 θ range from 10 to 60°, a continuous scan mode with a scan rate of 1° min⁻¹, and a step size of 0.03 for intensity integration. The measurements were taken at room temperature in the air at the normal pressure.

4.4.2 Sample Specification for XRD

RPCC aggregate samples were prepared by grinding and passing through a sieve number 200 and retain over sieve number 325. Each prepared sample was pressed into a plastic sample holder and properly labelled for identification.

4.4.3 Results

All RPCC samples showed the presence of small quantities of portlandite [Ca(OH)₂] and gypsum [CaSO₄ • 2 H₂O]. The gypsum would be due to its deliberate addition when the cement clinker is crushed. It is used to slow down the initial hydration process. The portlandite is the product of the hydration process in the cement paste. However, over the years, it would have been carbonated and reduced to 2 to 3%.

Appendix C contains charts for all samples represent the strongest intensity line for each compound. A typical presentation of the X-ray pattern is shown in Figure 4.4. The Figure shows the major components in the RPCC sample I-70#8 as peaks of calcite, dolomite and quartz. It can be interpreted as these minerals are in abundance in the sample. Table 4.3 compares the abundance of dolomite and calcite found from the thermal analysis data with the relative abundance of dolomite, calcite, and quartz as indicated from the X-ray diffraction data. It can be seen that the TG provides data on the abundance of dolomite and calcite while the X-ray provides data on dolomite, calcite, and quartz. Within these limitations, the data from TG-DTA and from XRD shows good agreement.

4.5 Leaching Experiment

A leaching experiment for laboratory is developed to simulate the effects of change of the aqueous environment surrounding the RPCC aggregates. In the leaching experiment, sample aggregates are immersed in deionised water and carbon dioxide gas is bubbled through the submerged aggregates. The carbon dioxide gas dissolves in the deionised water forming a weak carbonic acid that cause a change in pH and enhances dissolution of the calcium and magnesium ions present in the aggregates. The chemistry for this process is described in Chapter 1. In the natural process of events, the enhanced solutions of calcium and magnesium ions would deposit tufa upon:

- A change of pH when the “acidic solution” reaches an air interface and it loses CO₂.
- A change of temperature when the “acidic solution” is frozen and thawed.
- A change of concentration when evaporation occurs.

There are probably other conditions which would cause precipitation of the calcium ions in particular, but the above three changes represent the naturally occurring events. For the analysis of the enhanced calcium and magnesium contents of “acidic

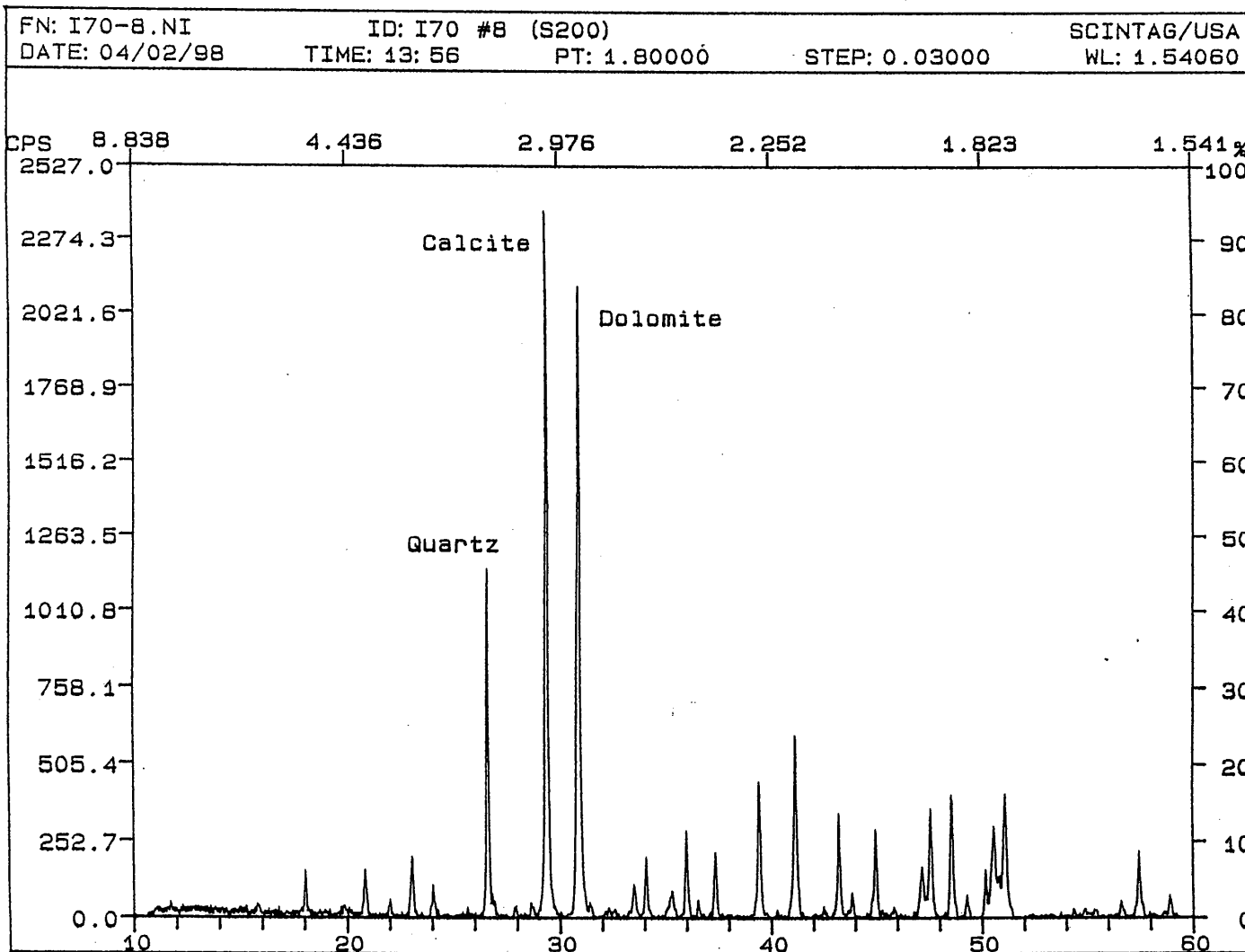


Figure 4.4: A typical XRD pattern for RPCC Aggregate Sample I-70#8 showing calcite, dolomite, and quartz (there are many peaks incorporated to characterize each compound. The peak cited here is the strongest intensity for such compound).

Table 4.3

Relative Abundance from TG-DTA and from XRD of the Components: Quartz (Q), Calcite (C), and Dolomite (D)

Sample ID	TG Data	XRD Data
I 70 # 1	D > C	D >>> C = Q
I 70 # 2	D >>> C (calcite low)	D >>> C > Q
I 70 # 3	D > C	Q > D > C
I 70 # 4	D > C	D > Q > C
I 70 # 5	D > C (C low)	D >>> C ≥ Q
I 70 # 6	D > C (C low)	D >>> Q = C
I 70 # 7	D only (C trace)	D >>> Q > C
I 70 # 8	D > C	C ≥ D > Q
I 70 # 9	D > C	D > C > Q
I 70 # 10	D > C	D > C > Q
I 70 # 11	D ≈ C (both low)	Q >>> D >>> C (trace)
I 70 # 12	D > C (both low)	Q >>> D >>> C (trace)
I 70 # 13	D > C (C trace)	Q >>> D >>> C (trace)
I 70 # 14	D > C (both low)	Q >>> D > C (low)
I 70 # 15	D > C (D low, C trace)	
I 70 # 16	D >>>> C (C trace)	
I 70 # 17	D > C (C low)	
I 70 # 18	D > C (C low)	
I 71 # 1	D > C	D > C > Q
I 71 # 2	C > D	C >>> Q > D
I 71 # 3	D > C	D ≈ C > Q
I 71 # 4	D >>> C (C trace)	D >>>> C > Q
I 71 # 5	D >>> C (C low)	D >>> C > Q
I 71 # 6	D > C (both low, C trace)	Q > D > C

I 71 # 7	C > D	C >>> Q > D
I 71 # 8	C > D	C >>> Q >>>> D (trace)
I 71 # 9	C > D	C >>> Q > D
I 75 # 3	D >> C (C low)	D >>>> Q = C
I 75 # 5	D >> C (C trace)	Q > D >> C
I 75 # 6	D >> C (C low)	D >>>> C >> Q
I 75 # 7	D >> C (C low)	
I 77 # 1	D > C	D >>>> C > Q
I 77 # 2	D > C (both low)	D >>>> C > Q
I 77 # 3	D >> C (C low)	D >>>> C > Q
I 77 # 4	D > C	
I 77 # 5	D > C (D low, C trace)	Q > D >>>> C
I 77 # 6	D > C (D low, C trace)	Q >>> D > C
I 77 # 7	D >> C (C trace)	D >>> Q > C
I 77 # 8	D only (D low)	Q = D (C trace)
I 90 # 1	D only	
I 90 # 2	D > C	
I 90 # 3	D > C (C low)	Q > D ≥ C
I 90 # 4	D > C (D low, C trace)	D > Q >>> C
I 90 # 5	D > C (both low)	Q > D >>> C
I 90 # 6	D >>> C (C trace)	Q > D >>> C

solution”, it is necessary to acidify the solution permanently by addition of nitric acid. This procedure is followed, namely aliquots of solution are withdrawn and immediately acidified with nitric acid. However the actual analysis is carried out using Inductively Couple Plasma - Atomic Emission Spectroscopy (ICP-AES).

4.5.1 The Equipment Design

For the leaching laboratory experiment a PVC pipe of 6 inches diameter and 12 inches long was taken to fabricate the apparatus. Both end of the pipe is capped with removable cap and two valves were fitted to the apparatus. The upper valve is for introducing CO₂ and the lower valve is for withdrawing leachate. Figure 4.5 shows a schematic diagram of the leachate apparatus. The design of the apparatus is inexpensive and easy to fabricate. Inside the cylinder, the upper valve is connected by a tube that carries CO₂ gas to a perforated ring at the bottom of cylinder. This provides the CO₂ gas bubbles up in the deionized water and mixes with the RPCC samples in the cylinder.

4.5.2 The Leaching Procedure

RPCC coarse aggregate samples passed through 1/2” sieve and retained on 3/8” were used for the leaching experiment. The sample is placed into the fabricated leaching apparatus and deionised water is added such that the sample is fully submerged. The ratio of RPCC aggregates sample to deionised water is 1:0.8 by mass. This provided that the water level is about 1” above the sample. The apparatus is closed with PVC cap. Carbon dioxide (CO₂(g)) is passed through the upper valve approximately at the rate of 800-900 mL min⁻¹. At the lower valve a nylon fabric was placed between the outlet valve and aggregate sample to prevent elution of fine suspended particles during withdrawal of water for leachate analysis.

The leachate for each sample is withdrawn at 24 hours after passing of the CO₂(g). Thereafter leachate is withdrawn at a regular interval. Each time 30-ml of the leachate is

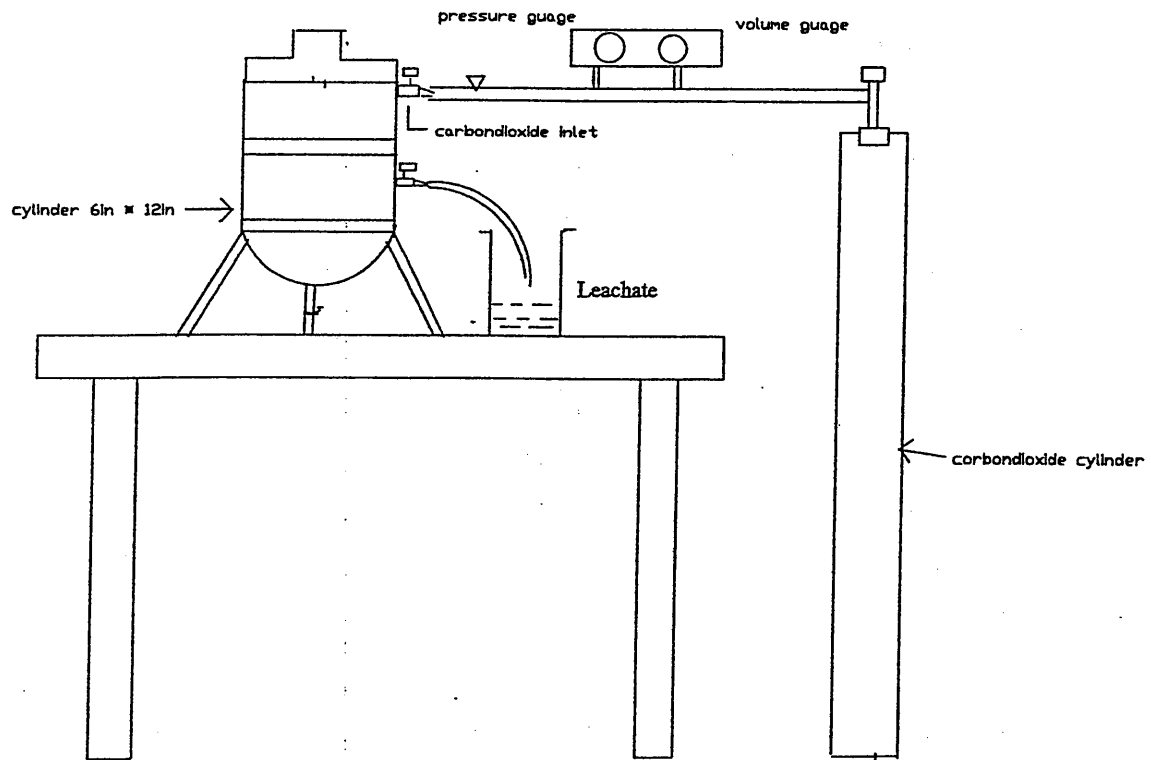


Figure 4.5 Schematic Diagram of Apparatus for the Leachate Experiment

withdrawn and filtered through a Nylon membrane filter (of 0.45 μm pore size) to ensure a clear solution. Nitric acids (HNO_3) of 20% strength is added drop by drop and mixed well until the pH of this solution reached 2 or lower to prevent the reprecipitation of calcium and/or magnesium ions in the solution. The sample solution is then kept in a tightly closed plastic (HDPE) container for further study.

4.5.3 Inductively Couple Plasma - Atomic Emission Spectroscopy (ICP-AES)

There are various analytical tools available for quantitative analysis of elements in rocks, sediments, metals, alloys, and solutions. In the present study, the atomic emission spectroscopy (AES) was selected on the basis of simplicity and less interference compared to flame atomic absorption spectroscopy. Moreover, AES has the capability to analyse multi-elements simultaneously and has a greater linear dynamic working range.

The inductively coupled plasma (ICP) is employed to estimate quantitatively an emission source. It is designed solely for liquid samples. There are three major instrument components, namely (i) plasma torch, (ii) Nebulizer, and (iii) spectrometer.

The plasma torch provides energy to atomise samples and to produce excited-state atoms. When the excited atoms return to their ground states, they emit their characteristic line spectra. A plasma is a gas containing a significant fraction of its atoms and molecules in an ionised state. Argon gas is a usual source of plasma. The plasma can interact with magnetic fields. The inductive coupling of a time-varying magnetic field is the basis of the operation of an ICP torch.

The liquid samples must be introduced into the plasma as very small droplets. This is made possible by the use of a nebulizer. A peristaltic pump is employed to pump the liquid samples to the nebulizer. The sample solutions must be free of particulate

matter or solid particles. In addition, when introducing a high concentration of dissolved salts, special care must be exercised to prevent the clogging of the nebulizer nozzle.

An atomic emission spectrometer is used to characterize the signals as many elements can be measured simultaneously or rapidly sequentially. The simultaneous instrument is suitable for faster analyses in routine work while the sequential instrument (used in this project) is designed for research work having a large variation in elemental compositions.

4.5.3.1 Equipment and Procedure

The instrument used in this research project to investigate the concentration of calcium and magnesium ions is "Perkin Elmer Plasma II Emission Spectroscopy". High purity (>99.99%) argon gas is employed as a plasma source in the investigation. The detection wavelength for magnesium ions is 280.270 nm and for calcium is 396.847 nm. A Xenix operating system with Plasma1000/2000 software version 1.10 is used as a data acquisition tool. Appendix D provides the instrument operating parameters and chemicals used in sample preparation for ICP-AES experiment.

For the ICP-AES experiments known concentrations of calcium and magnesium ions are needed. Therefore, a series of standard solutions containing both calcium and magnesium ions were prepared for a calibration curve. The calibration curve is useful to identify the emission intensities to the element concentrations. Concentrations of the standard solutions were prepared to cover the entire range of the sample (leaching) solutions. Table 4.4 shows the six standard solutions that were prepared to cover the entire range concentration of Ca^{2+} and Mg^{2+} ions in ppm. One percent of lanthanum solution was added to prevent chemical interference from phosphate and aluminium ions that may have leached out into the leaching solution.

4.5.4 Leachate ions concentration Results

It was observed that the calcium ions concentration reached its saturation at approximately 24 hours after passing CO₂ gas through the submerged RPCC aggregates samples. After 24 hours time, the magnesium ions concentration has substantially increased while the calcium ions concentration has dropped. This shows the “common ion effect” in which these two ions compete each other to dissolve in the solution. Table 4.5 shows Ca²⁺ and Mg²⁺ ions concentration for each RPCC sample obtained from the leachate after passing CO₂ gas for 24 hours. The Table also shows a ratio of Mg/ Ca concentration. The Mg/ Ca ratio for most of the RPCC sample is below 0.6 except few samples as noted in the Table 4.5. Figure 4.6 shows the plot of the concentration of calcium and magnesium ions in the leachate solution for sample I-90 # 1. It shows the concentration from three hour to 103 hours after the passing of CO₂ (g). It indicates that initially the concentration of Ca ions is higher than Mg ions. As time passes, it reaches to an equilibrium condition and then Ca ion concentration reduces as compared to Mg ions.

Table 4.6 shows the ICP analysis results for rubblized concrete and 304 samples. The rubblized concrete samples show a ratio of Mg/Ca less than 0.6 which indicates that the calcium ions in the concrete has carbonated and there is less likelihood that it will precipitate as tufa. It is certainly obvious due to the fact the concrete is 30+ years old. The 304 samples show calcium ions are higher in fine aggregates as compared to coarse aggregates. Both fine and coarse aggregates have Mg/Ca ratio higher than 0.6 indicating that here is higher possibility of carbonate leaching.

Figure 4.7 shows a plot of calcium and magnesium ions concentration in ppm (part per million) in leachate for the sample I-70 # 1 through 16. The leachate sample was drawn at 24 hours after passing CO₂ (g). A similar plot for sample I-90 # 1 through 6 is shown in Figure 4.8. An analysis of the observations presented in these two figures indicates that leachate of each sample shows a higher concentration of calcium ions as

Table 4.4

The Concentration of the Standard Solution used for the Calibration Curve

Standard Solution #	Ca ²⁺ / ppm	Mg ²⁺ / ppm	% Lanthanum Sol.
Standard Solution # 1	1.0	1.0	1
Standard Solution # 2	5.0	5.02	1
Standard Solution # 3	10.0	10.04	1
Standard Solution # 4	20.10	20.08	1
Standard Solution # 5	50.25	50.20	1
Standard Solution # 6	100.50	--	1

Table 4.5

Calcium and Magnesium Ions Concentration in parts per million obtained after passing CO₂ for 24 hours.

A. RPCC Sample from I-70.

Sample ID	Mg (ppm)	Ca (ppm)	Mg/Ca
I-70#1	251.84	724.53	0.347
I-70#2	408.57	540.11	0.757*
I-70#3	420.27	512.69	0.819*
I-70#4	223.82	546.85	0.41
I-70#5	295.77	502.88	0.59
I-70#6	267.25	423.59	0.632*
I-70#7	342.57	486.57	0.704*
I-70#8	123.33	627.97	0.196
I-70#9	306.56	542.24	0.565
I-70#10	217.38	578.02	0.375
I-70#11	252.96	609.96	0.414
I-70#12	36.23	628.63	0.057
I-70#13	58.11	992.26	0.058
I-70#14	85.22	903.55	0.094
I-70#15	137.44	838.89	0.164
I-70#16	130.78	716.12	0.182
I-70#17	102.95	442.04	0.233

*Ratio of Mg/Ca > 0.60

Table 4.5 Continued

B. RPCC Sample from I-71.

Sample ID	Mg (ppm)	Ca (ppm)	Mg/Ca
I-71#1	235.04	418.27	0.5617
I-71#2	212.32	497.62	0.427
I-71#3	231.91	466.85	0.497
I-71#4	197.31	396.32	0.50
I-71#5	207.61	498.01	0.418
I-71#6	217.01	397.36	0.546
I-71#7	206.31	298.66	0.6944*
I-71#8	293.40	341.16	0.8620*
I-71#9	190.05	387.85	0.4901

*Ratio of Mg/Ca > 0.60

C. RPCC Sample from I-75.

Sample ID	Mg (ppm)	Ca (ppm)	Mg/Ca
I-75#1 [#]	-	-	-
I-75#2 [#]	-	-	-
I-75#3	303.61	468.96	0.649*
I-75#4 [#]	-	-	-
I-75#5	187.61	449.81	0.418
I-75#6	228.36	419.81	0.546
I-75#7	218.66	367.41	0.595

#: Samples not received.

*: Ratio of Mg/Ca > 0.60

Table 4.5 Continued

D. RPCC Sample from I-77.

Sample ID	Mg (ppm)	Ca (ppm)	Mg/Ca
I-77#1	216.50	477.61	0.454
I-77#2	212.31	467.66	0.454
I-77#3	203.41	398.41	0.5128
I-77#4	248.66	200.48	1.250*
I-77#5	233.61	309.33	0.757*
I-77#6	230.61	437.61	0.529
I-77#7	246.11	406.31	0.606*
I-77#8	200.12	467.66	0.429

*: Ratio of Mg/Ca > 0.60

E. RPCC Sample from I-90.

Sample ID	Mg (ppm)	Ca (ppm)	Mg/Ca
I-90#1	370.20	646.90	0.574
I-90#2	93.90	659.95	0.142
I-90#3	95.25	682.65	0.139
I-90#4	80.60	680.13	0.118
I-90#5	113.63	679.90	0.167
I-90#6	132.15	607.90	0.217

*: Ratio of Mg/Ca > 0.60

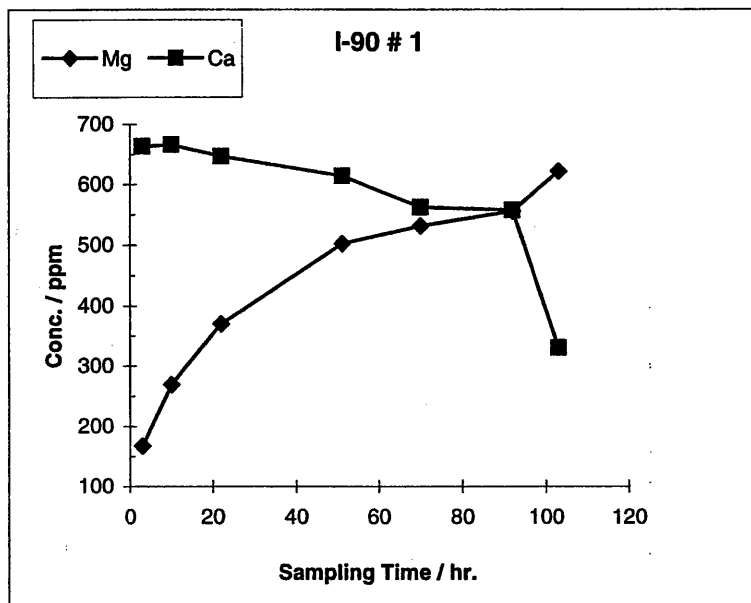


Figure 4.6 A Plot of the Concentration of Calcium and Magnesium Ions in the Leachate Solution vs. The Sampling Time for Sample I-90 #1.

Table 4.6

ICP Analysis Results for Rubblized Concrete and 304 Samples

Sample #	Calcium Concentration in (ppm).	Magnesium Concentration in (ppm).	Mg/Ca
RC-1	22.56	5.76	0.25
RC-2	29.63	5.21	0.17
RC-3	47.15	3.12	0.07
RC-4	11.69	4.40	0.38
304 (Fine Aggregate)	519.10	352.92	0.68
304 (Coarse Aggregate)	315.79	335.95	1.06

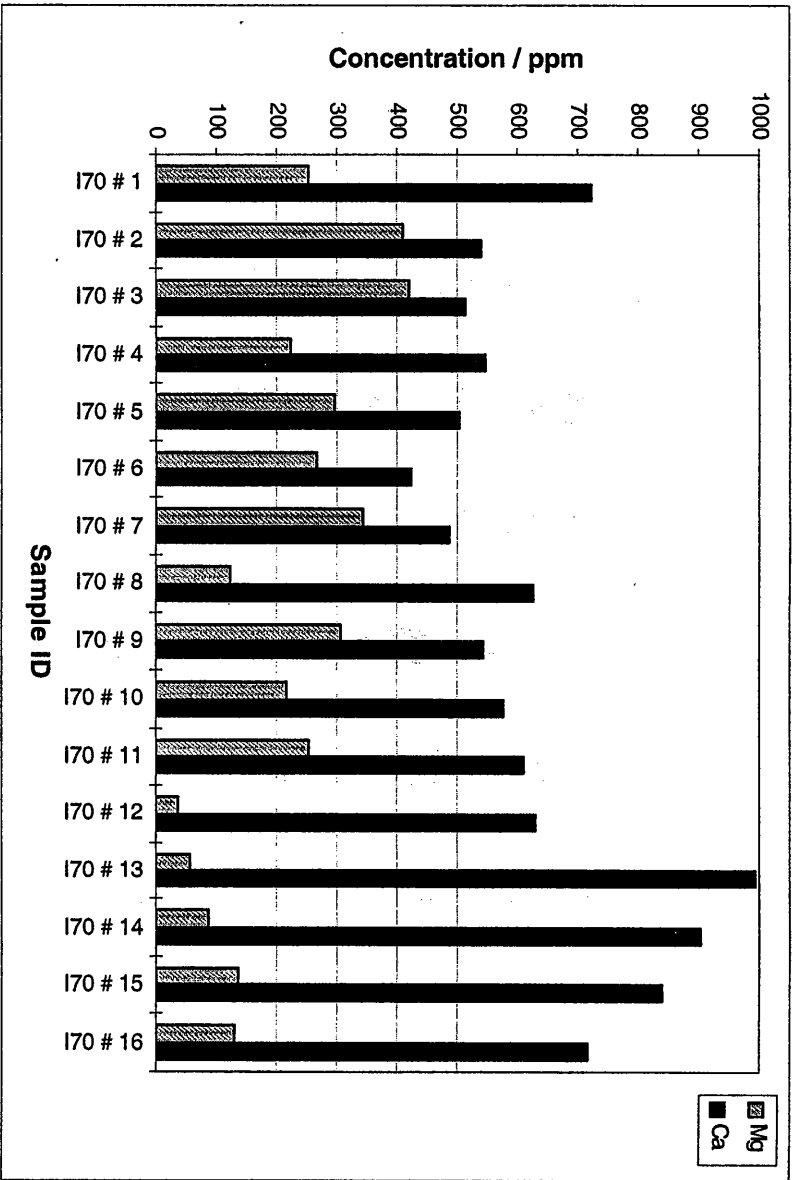


Figure 4.7: A Plot of the Concentration of Calcium And Magnesium Ions Determined from Leachate Solutions for Sample I-70 Sampling @ 24 hours

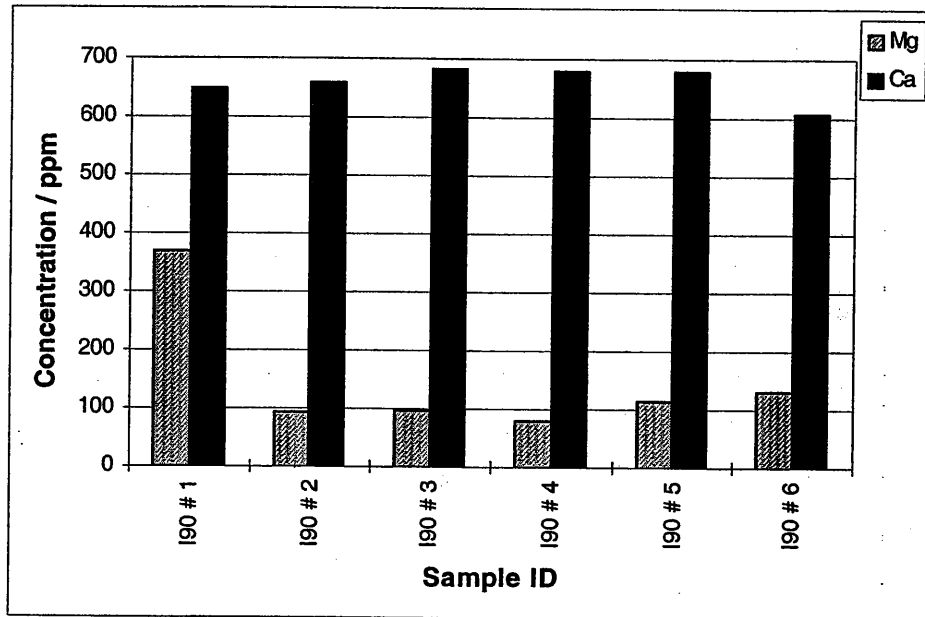


Figure 4.8: A Plot of the Concentration of Calcium And Magnesium Ions Determined from Leachate Solutions for Sample I-90 Sampling @ 22 hours

compared to magnesium ions. A high concentration of calcium ions is seen in samples I-70 # 12 through 16 and I-90 # 2 through 6 as compared to magnesium ions. This shows and confirms the "common ion effect". Further investigation of the attribution of the calcium ions toward the formation of tufa can easily be performed by measuring the calcium and magnesium ions in the leachate solution left in a container under ambient condition. It was found that, after 2 month in an open container, the calcium ion concentration dropped from around 700 ppm to 2 ppm. This indicates that calcium ions combined with CO_2 (g) is precipitated as CaCO_3 i.e. tufa.

Figure 4.9 shows plots of calcium and magnesium ions for samples I-70 # 7, 11, 12, 14 and I-71 # 2, 6 with the presence of CO_2 (g) atmosphere for 24 hours and the absence of CO_2 (g) atmosphere for 72 hours. Separately it was observed that without the supply of CO_2 (g), the pH of the leachate solutions increased from approximately 6.4 to 11.6. In this environment, the dissolution of both magnesium and calcium ions has sharply decreased, especially the calcium ions. The change of pH occurs naturally as the (acid) rain subsides and/or the drainage water reach the surrounding environment, i.e. farm land.

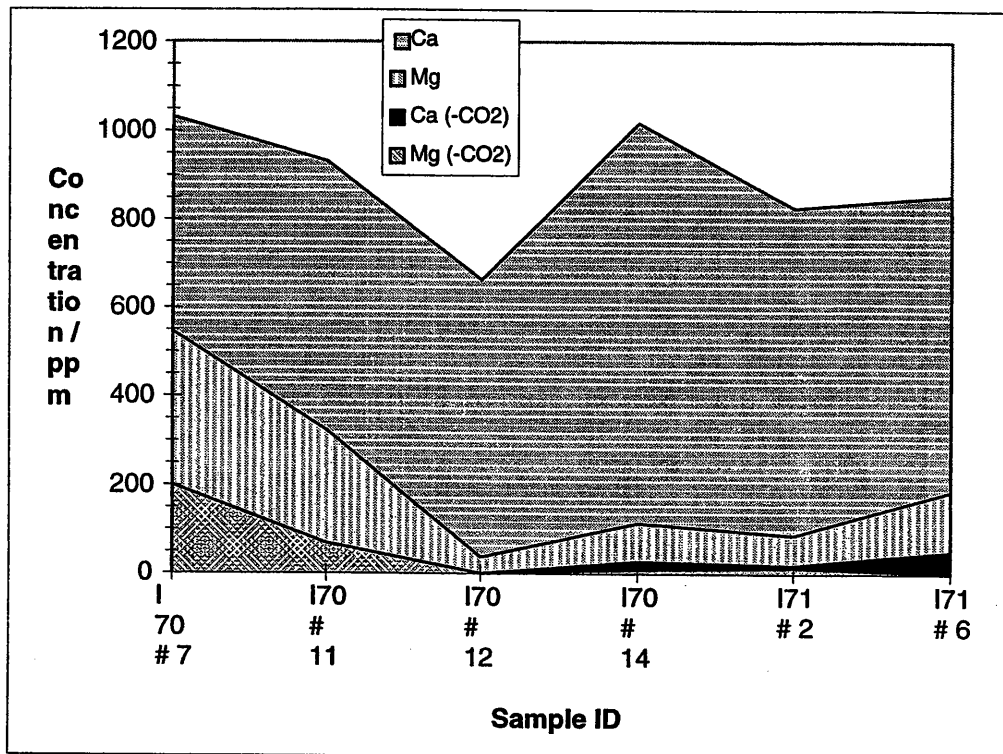


Figure 4.9: A Plot of the Concentration of Calcium and Magnesium Ions Determined from Leachate Solutions for Samples of I-70 and I-71. Sampling with the presence of CO₂ (g) for 24 Hours and the absence of CO₂ (g) for 72 hours.

Chapter 5

Tufa Formation

5.1 Introduction

In this chapter, the formation of tufa in drainage situations is examined. Other laboratory experiments in which tufa is formed are also described. The influence of container surface in causing the precipitate is noted. Generally, tufa formation is due to excess dissolution of calcium ions by alteration of the pH caused by absorption of carbon dioxide into the aqueous solution. Then, one of the conditions already discussed must exist to form tufa:

- change of pH,
- evaporation, and
- change to temperature (freezing and thawing).

The change of condition will bring about the precipitation of tufa. There is a kinetic factor, which has not been studied quantitatively as the nature of the surface of container holding the Ca^{2+} ions solution influence the precipitation is varying in field. In the real world condition actual sites, the nature of the drainage system will induce the tufa precipitation. Some of the factors that induce are:

- drainage velocity,
- gradient of the drainage system, and
- material used in the drainage system.

The experiments described in this chapter are an initial look into these factors.

5.2 The Sugar Test (Ethylene Glycol Test)

The “sugar test” is designed to determine free lime (CaO). RPCC aggregates that contain slag as a component for aggregates may pose a real danger due to the existence of free calcium oxide. This was found in a previous study on slag components [23], however, in the present study the RPCC aggregates samples would have an aging effect. Any free calcium oxide present would have weathered over the thirty years lifetime of the samples. The weathering consists of hydration to portlandite through action of moisture, and direct carbonation through the action of carbon dioxide dissolved in water.

The determination of free lime, reported by Schlapfer and Bukowski [24, 25] is a simple method based on the extraction of CaO in ethylene glycol heated at 70°C. This method has been evaluated by Javellana and Jawed [26] for CaO determination and compared to the ASTM method. They concluded that the Ethylene Glycol test is preferable to the ASTM on the ground of simplicity and is less time consuming. Appendix E provides the procedure of Ethylene Glycol test, apparatus and chemicals used. Figure 5.1 shows a system flow chart for the determination of percent free lime through Ethylene Glycol test.

5.2.1 Ethylene Glycol (Sugar) Test Results

A few RPCC samples were selected for the sugar test. It was found that only minute or negligible amount of free calcium oxide is present in each sample. In view of the age of the samples, this is not surprising. The results (mean values from triplicate runs) are given in Table 5.1. It shows that the percentage of Free lime in all but one sample is less than 1 percent. In the previous study [1] it has been demonstrated that one percent value of free lime present in aggregate is critical in the production of tufa. For comparison purpose of free lime, washed sea sand (lot # 880642, Fisher Scientific Co.) was used as a blank. Only sample ID # 170-11 showed that it contains 1.55 percent of free lime that is greater than 1 percent. On the basis of

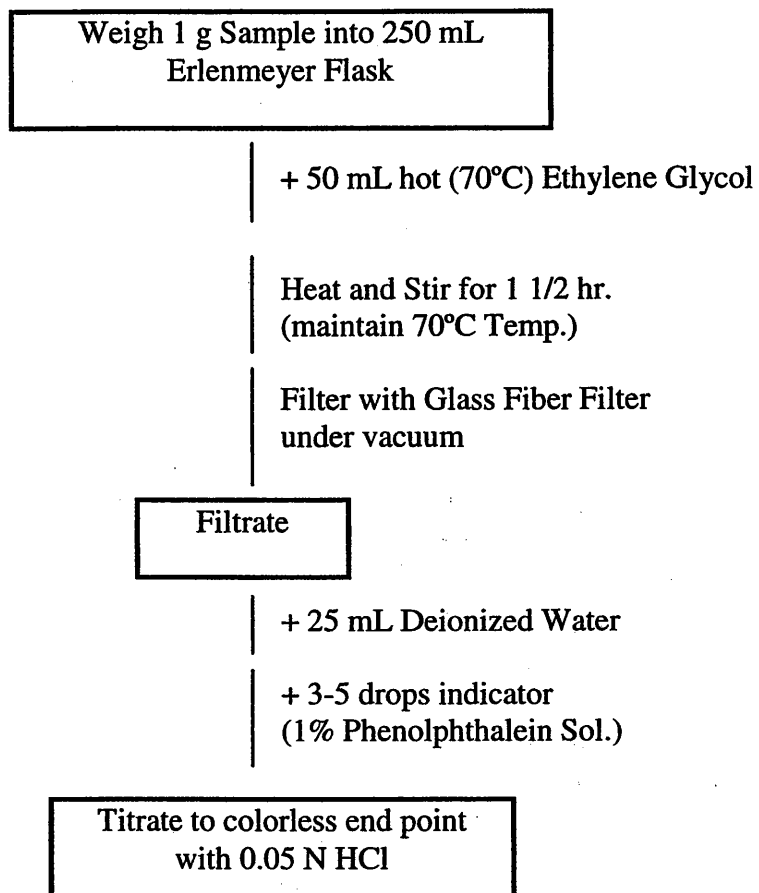


Figure 5.1: A System Flow Diagram to Determine Percent of Free Lime through Ethylene Glycol Test

Table 5.1**Experimental Results of Ethylene Glycol Test for RPCC samples.**

Sample#	% CaO	Sample#	% CaO
I-70#1	0.7900	I-71#8	Neg
I-70#2	Neg	I-71#9	Neg
I-70#3	0.865	I-75#1	-
I-70#4	0.785	I-75#2	-
I-70#5	0.375	I-75#3	Neg
I-70#6	0.340	I-75#4	-
I-70#7	0.50	I-75#5	Neg
I-70#8	Neg	I-75#6	Neg
I-70#9	0.35	I-75#7	Neg
I-70#10	Neg	I-77#1	Neg
I-70#11	1.545*	I-77#2	Neg
I-70#12	0.585	I-77#3	Neg
I-70#13	0.390	I-77#4	Neg
I-70#14	0.470	I-77#5	Neg
I-70#15	Neg	I-77#6	Neg
I-70#16	Neg	I-77#7	Neg
I-70#17	Neg	I-77#8	Neg
I-71#1	0.88	I-90#1	Neg
I-71#2	0.815	I-90#2	Neg
I-71#3	0.535	I-90#3	Neg
I-71#4	Neg	I-90#4	Neg
I-71#5	Neg	I-90#5	Neg
I-71#6	Neg	I-90#6	Neg
I-71#7	Neg		

Neg: Negligible

*: Higher than 1%

previous study [1] it can be concluded that as majority of samples contain less than 1 percent of free lime, hence it is unlikely that they may contribute in precipitation of tufa.

5.3 Analysis of Samples from Under-drains on Project 332-97

During the course of the research project, ODOT has supplied two under drain samples from project 332-97 and requested to conduct XRD and other physico-chemical tests to evaluate for tufa precipitation. The first sample is in a form of pebbles cemented with tufacious material and another sample is in a form of a yellowish powder. The following tests were performed on these samples:

Experiment / Work	Pebbles coated with tufacious material	Powdery material
SEM	+	+
EDS	+	+
XRD	N/A	+

+ indicates tests were performed;

N/A not available

5.3.1 Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer (SEM-EDS)

The experiments were performed on JEOL JSM-6100 Scanning Electron Microscope with Link Energy Dispersive X-ray Spectrometer. The software for EDS analysis is Link Analytical EXL.

The samples were mounted onto double-sided glue tape placed onto the graphite disc. DENTON VACUUM DESK II was used as a coating device with a pressure of 40 millitore, and palladium/gold (Pd/Au) cathode was utilised as coating source.

For SEM, Polaroid film No. 52 and/or 53 was used to record the morphology of the samples. Energy supply, magnification, and working distance (WD) were recorded onto the photomicrograph (see Photograph 5.1). The Scanning Electron Microscope (SEM) reveals the surface characteristics and shape of the RPCC powder. In addition, it is possible to characterize the elemental composition of the sample surface by the use of the Energy Dispersive Spectrometer (EDS) data associated with the SEM.

The EDS peaks for each element can be seen in the Figures 5.2 and 5.3 for pebbles and power sample, respectively. It should be noted that Palladium (Pd) and Gold (Au) signals shown in both figures came from the sample preparation process (coating) not from the original sample itself. The major elements on the surface of pebbles sample are: Ca, Si, Mg, and Al. The major elements on the powdery sample are: Ca, Si, Mg, Al, Fe, Zn, Na, and K. This technique is complimentary to XRD and the results are in good agreement.

5.3.2 X-ray Powder Diffraction (XRD)

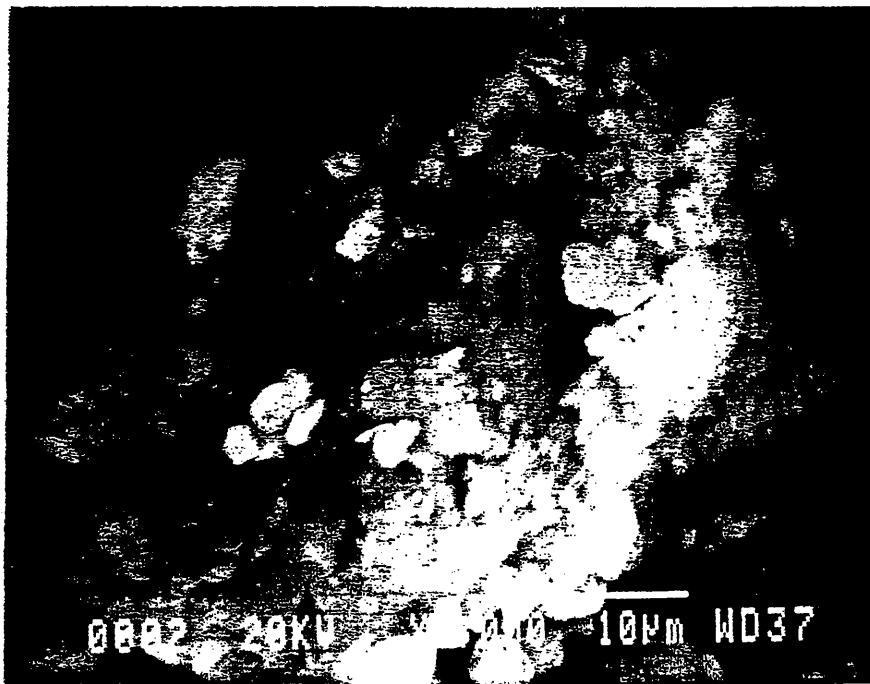
For the XRD experiment the sample was grounded using porcelain mortar and pestle. It was passed through Nylon sieve no. 200 and stored in a plastic sample holder. The sample was analysed for its constituents. It was found that the sample contains almost entirely (> 92%) CaCO_3 in the form of calcite with a small amount of quartz (SiO_2) as seen in the Figure 5.4

5.3.3 Discussion

The sample containing pebbles are observed as cemented together with a cementitious layer of calcite. The calcite is formed from supersaturated solutions of calcium ions present

when acidic rainwater passes through beds of limestone or RPCC used in proximity to the drainage system. The pebbles form a suitable nucleating surface for the re-deposition of calcite leading to an adhering mass of pebbles.

The other sample containing powdery material is calcite of an impure variety. It is formed by the same process as above and forming a deposit in the drainage system.



Photograph 5.1: SEM Photograph for Under-drain Sample (Project 332-97)

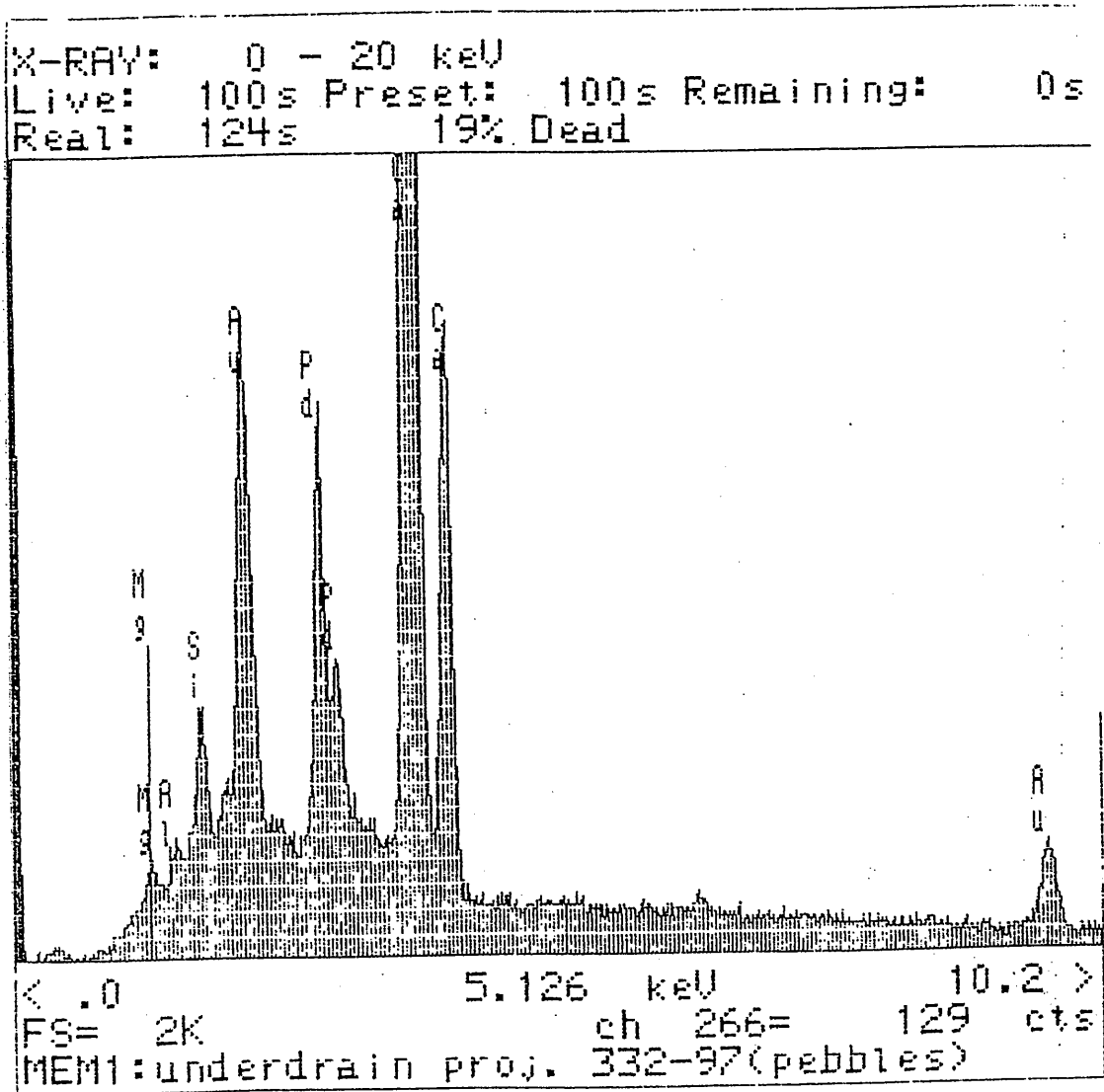


Figure 5.2: The EDS plot for sample from under-drains on project 322-97 (Pebbles)

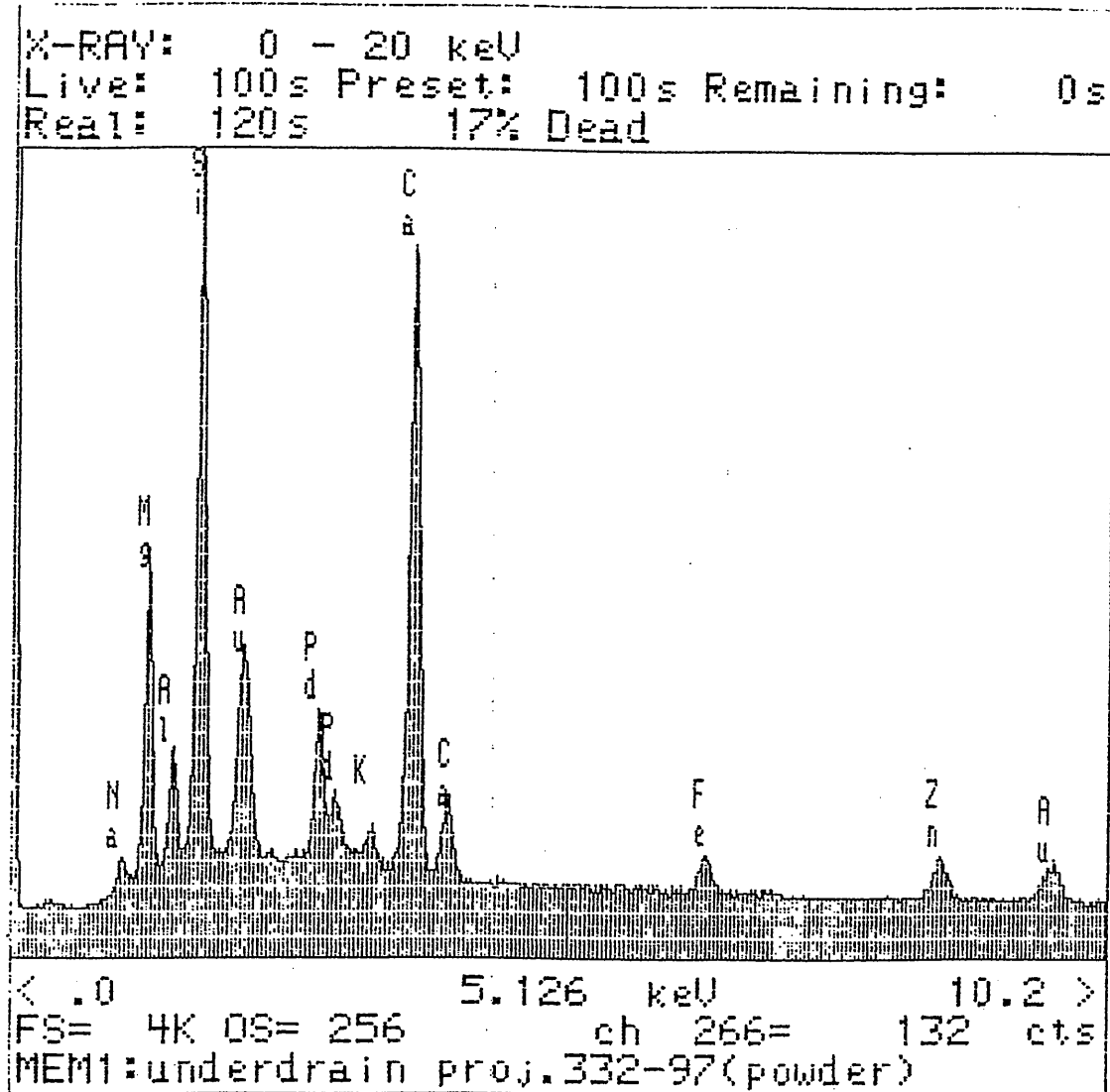


Figure 5.3: The EDS plot for sample from under-drains on project 322-97 (Powder)

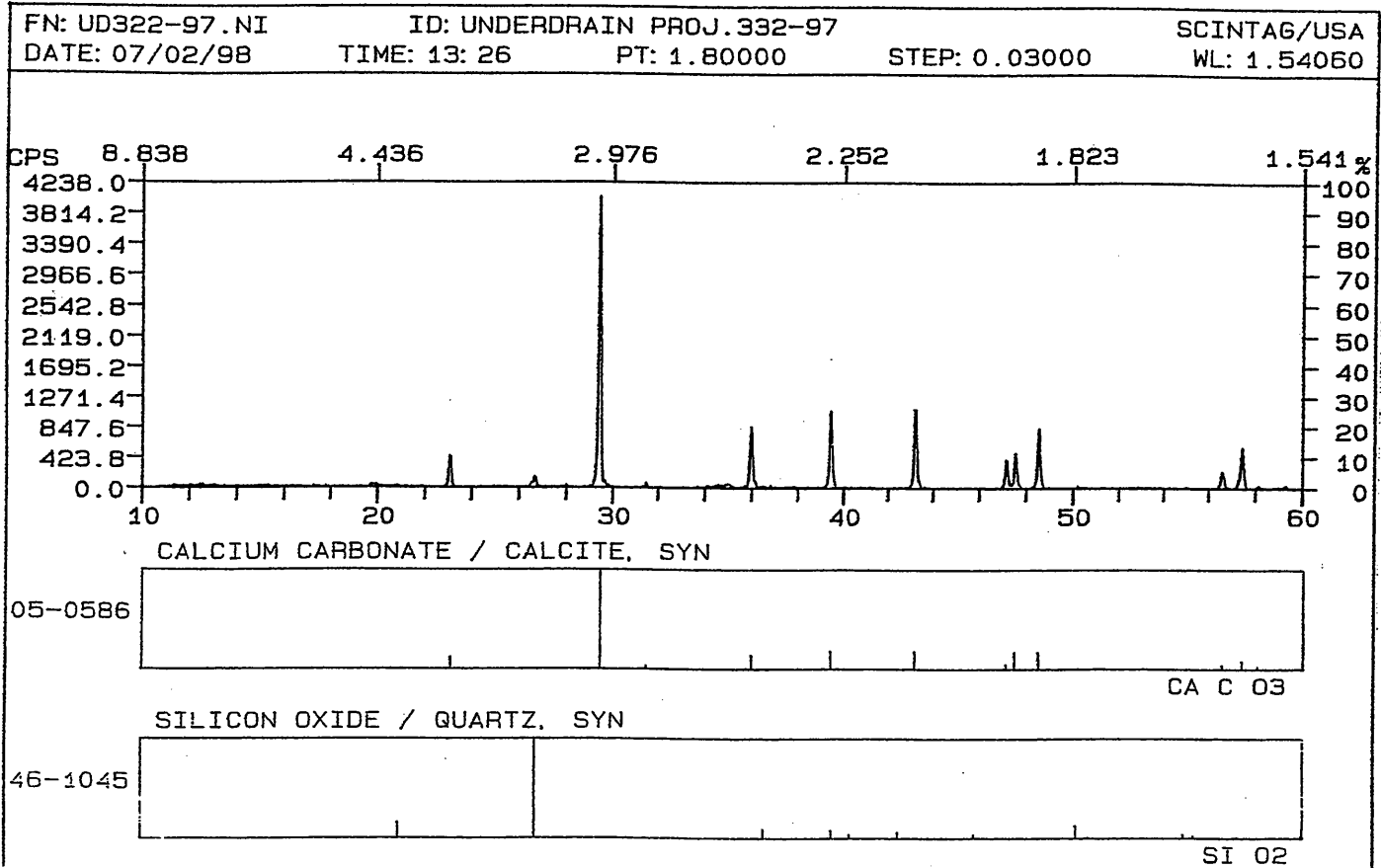


Figure 5.4: The XRD Pattern for Sample from Under-drains on Project 332-97 showing the sample pattern and the standard pattern

Chapter 6

Analysis, Discussion, Conclusions and Recommendations

6.1 Review of Experimental Procedure

The present research is confined to a study of Recycled Portland Cement Concrete (RPCC) aggregates which are over 30 years old and are used or are to be used as base or sub-base in road construction. In this respect, it should be noted that these aggregates are derived from RPCC rigid pavement of interstate highways in the state of Ohio. Their use as a base or sub-base aggregates would be to replace virgin aggregates commonly used for this purpose. Also their use would help in managing waste materials and stock piling. In the field and in the laboratory, leaching occurs when such RPCC aggregates are subjected to acidic water (defined here as carbon dioxide dissolved in water), and increased quantities of calcium and magnesium ions entered into solution.

In the present study, the location of RPCC aggregates is described. The RPCC aggregate samples made up of coarse and fine aggregates and cement. The aggregate consisted of mixtures of calcitic limestone, dolomitic limestone, and quartz. Occasionally, slag was also used. The technique of thermal analysis has shown that portlandite, calcite, and dolomite were present in all RPCC aggregates samples. The technique enabled the establishment of percentage present of portlandite, calcite, and dolomite. It also showed the presence of quartz. Whereas the X-ray powder diffraction studies enabled the relative abundance of calcite, dolomite, and quartz to be established. The leachate experiments showed that in acid rain the solutions contained supersaturated amounts of calcium and magnesium ions which could be re-precipitated under various naturally occurring conditions.

When the study was first started, the question was which RPCC aggregates would show excessive leaching of calcium and magnesium ions. The laboratory tests showed

that supersaturated solutions of calcium and magnesium ions formed in every leaching test. Then question still remains why precipitation of tufa occurs in some localities and not in all locations as was reported in previous study. As discussed in chapter 5 that there are other reasons such as surface of container, gradient, velocity, temperature, and so on for precipitation to occur.

6.2 Thermal Analysis

The equipment used was a Simultaneous TG-DTA unit. The DTA enabled the presence of quartz to be established. The runs in carbon dioxide revealed the presence and percentage of portlandite, calcium carbonate, and dolomite to be calculated. However, the portlandite $[\text{Ca}(\text{OH})_2]$ over the span of 30 years will have largely carbonated. Instead of the usual range of portlandite from 10-20 percent [3] found in newly hydrated concrete, the amount present was around 5 percent. The calcium carbonate data was the sum total of calcium carbonate formed from the carbonation of the portlandite, and the use of calcitic limestone as an aggregate.

The chemistry of the reactions occurring in the heat treatment is explained in Chapter 1 and the method of calculation based on the thermal analysis are reported in Chapter 4 and the Appendix B. The results showed that dolomite was present in all samples indicating its use as aggregate. On the other hand, calcitic limestone was found to be very low or absent in certain RPCC aggregates in spite of the carbonation that must have occurred due to the weathering of portlandite over 30 years.

6.3 The X-ray Powder Diffraction Data

The X-ray Powder Diffraction data showed the relative abundance of calcite, dolomite, and quartz and in general confirmed the findings reported from the thermal analysis experiments. The expected small amounts of portlandite and gypsum could be

detected in all samples. Overall, the predominant use of dolomite as an aggregate was confirmed.

6.4 The Leaching Experiments

The use of the ICP-AES equipment showed that in all experiments the presence of carbonic acid water caused excessive amounts of calcium and magnesium ions to be leached out into solution. However, the tests showed that over a period of time as the magnesium ion concentration increased the calcium ion concentration decreased (see Figure. 4.6). There was other evidence of the concentration of calcium and magnesium ions being related. There is a need to investigate further the manner in which the tufa is precipitated and the destination of the magnesium ions while the tufa is being deposited. The causes of the reprecipitation remain as already stated in the Chapter 4 on leaching, namely:

1. Change of pH from acid to near normal at the air/water interface when there is a drastic change in solubility.
2. A change of temperature to cause a freeze-thaw effect.
3. Evaporation of the solution.

All these events are naturally occurring phenomena, and could quantitatively be demonstrated by setting up a test-tube experiments. However, the precipitation was often gelatinous and not a clearly defined particulate material indicating that factors of particle growth, listed as nuclei formation, growth of nuclei and growth obstruction need to be studied. Blockage of the drains with tufa would seem to indicate that adhesion to container walls or between coarse stones plays an important role in the process of precipitation of tufa.

6.5 Overall Discussion

A broad conclusion could be derived that the amount of tufa precipitation can be affected from acid solutions (CO_2 in water) which is a naturally occurring changes. The nature of the precipitate of tufa varies according to the conditions imposed on the system and a great deal of work is needed in this area. The fact remains that a danger exists of reprecipitation of tufa in all the RPCC aggregates investigated in the present study. Table 6.1 shows Mg/Ca ratio for all RPCC samples by aggregate types and ambient temperature. In the literature, it was shown that there is a highly likelihood of tufa precipitation if a ratio of Mg/Ca is higher than 0.6. A critical review of the Table 6.1 suggests that there are nine RPCC samples out of total of 44 samples have a higher ratio of Mg/Ca. These nine RPCC samples are distributed across aggregates types and ambient temperature. It also indicates that the ambient temperature below 50°F , at the time of placing of concrete has a higher effect on tufa precipitation.

The calcium ions that enter into solution under acidic conditions come from the portlandite, the calcitic limestone, and dolomite. The literature suggests that the smaller the particle size of the RPCC aggregates, the greater will be the tendency to produce both calcium and magnesium ions into solution in the presence of acid water. This effect was generally noted throughout the present study. The friability of the RPCC aggregates and the amount of "fines" present would seem to be of great importance and needs to be studied further. However it is certainly advantageous to limit the RPCC aggregates size to coarse aggregates for use as base and subbase aggregates. To reduce the amount of precipitation, it is a good practice to not use fine aggregates.

Super-saturation of calcium and magnesium ions occurred in all leachate solutions examined under acidic conditions. However, in road construction, formation of tufa is limited to a few localities. The details of engineering in drainage system construction would seem to be an important factor in future studies on this subject.

Table 6.1

Mg/Ca Ratio for RPCC Project by Aggregate Types and Ambient Temperatures

Sample#	Gravel			Limestone			Slag		
	Below 50°F	Between 50°F-70°F	Above 70°F	Below 50°F	Between 50°F-70°F	Above 70°F	Below 50°F	Between 50°F-70°F	Above 70°F
I-70#1		0.347							
I-70#2			0.757*						
I-70#3	0.819*								
I-70#4					0.41				
I-70#5		0.59							
I-70#6	0.632*								
I-70#7			0.704*						
I-70#8				0.196					
I-70#9						0.565			

I-70#10				0.375					
I-70#11						0.414			
I-70#12	0.057								
I-70#13								0.058	
I-70#14							0.094		
I-70#15								0.164	
I-70#16							0.182		
I-70#17							0.233		
I-71#1	0.5617								
I-71#2		0.427							
I-71#3			0.497						
I-71#4					0.50				
I-71#5						0.418			
I-71#6								0.546	
I-71#7									0.6944*
I-71#8							0.8620*		
I-71#9							0.4901		
I-75#1	-								

I-75#2			-						
I-75#3	0.649*								
I-75#4			-						
I-75#5						0.418			
I-75#6				0.546					
I-75#7					0.595				
I-77#1						0.454			
I-77#2		0.454							
I-77#3		0.5128							
I-77#4					1.250*				
I-77#5								0.757*	
I-77#6									0.529
I-77#7									0.606*
I-77#8				0.429					
I-90#1									0.574
I-90#2						0.142			
I-90#3					0.139				
I-90#4				0.118					

I-90#5								0.167	
I-90#6									0.217
Number of Samples with Mg/Ca > 0.6	3	-	2	-	1	-	1	1	1
Number of Samples in each Category	5	5	3	5	5	6	5	5	5

* indicates Mg/Ca ratio > 0.60

Summary of Table 6.1

Pouring Temperature	< 50⁰ Fahrenheit	50⁰ - 70⁰ Fahrenheit	> 70⁰ Fahrenheit	Total Number of Samples
Number of Samples	15	15	14	44
Mg/Ca Ratio	4	2	3	9

6.6 Conclusions

The conclusions of the current research reflect the acceptability criteria for RPCC aggregates to be used as base or subbase courses.

1. Research conducted earlier by Narita, et.al [27] had established that aggregates with free lime content (CaO) more than 1% must not be used as base or subbase courses, as they release calcium ions immediately into solution. In the analysis conducted for the samples, only sample I-70#11 had free lime content more than 1%. All other samples have free lime less than 1% (Table 5.1).
2. From the leachate experiments, it was widely evident that magnesium ion concentration in solution increased with time and calcium ion concentrations in solution reduced with time. It indicates the common ion effect, where magnesium shows the tendency to be in dissolved state, thereby reducing the solubility of calcium ions in solution (i.e. calcium ions combined with carbonate ions are precipitated as calcium carbonate). A ratio of $Mg/Ca = 0.60$ [8] indicates that the solution is saturated with respect to calcium ions, and if the same ratio is above 0.60, then the solution is supersaturated with respect to calcium ions and that will result in the precipitation of calcium carbonate or tufa. The leachate experiments were showed, nine samples had Mg/Ca ratio more than 0.60. They are I-70#2, I-70#3, I-70#6, I-70#7, I-71#8, I-75#3, I-77#4, I-77#5, I-77#7. Thus, it indicates that there is a highly likelihood that will have a higher tufa precipitation as compared to others.
3. The ambient temperature at the time of construction is below 50°F, has a higher effect on tufa precipitation.

6.7 Recommendations

On the basis of the study of RPCC aggregates the following broad assumptions are suggested to reduce the potential of tufa formation:

1. Use of RPCC aggregates should be limited to coarse aggregate size only.
2. Determine Mg/Ca ions ratio by the ICP-AES analysis carried on the leachate (obtained as a result of passing CO₂ through the RPCC aggregates). Limit the use of RPCC aggregate to a ratio of less than 0.60.
3. Determine the free lime present in the RPCC aggregate (using Ethylene Glycol Test) and limit the use of RPCC aggregate to one percent or less. However, RPCC aggregates have already aged over thirty years, then it is unlikely to detect percent of free lime over one percent.

6.8 Future Studies

1. The rate of release of calcium and magnesium ions into solution is a function of the extent of the presence of calcium and magnesium-bearing minerals in RPCC aggregates. Magnesium ions are released from the mineral dolomite. Whereas, calcium ions are released from the minerals dolomite, calcite and portlandite. These minerals are all present in RPCC aggregates along with a cement-sand matrix. In the current research, all the RPCC samples were tested in identical conditions. Future research may be needed to focus on the rate of release of calcium and magnesium ions from RPCC samples under varying conditions of pH, temperature, etc.
2. Blending of aggregates needs to be taken up for the reduction of leaching of calcium ions into solution. Literature indicates that the presence of a few calcium-attenuating

minerals can substantially reduce the possibility of precipitation of tufa. Research may be conducted to evaluate the blending of calcium-attenuating minerals with high-calcium RPCC aggregate to study the reduction of calcium ions into solution.

3. Dolomitic limestone is considered to undergo chemical dedolomitization (due to interaction between aggregate and concrete paste) and physical dedolomitization (due to grinding), thereby resulting in an increase in its surface area. The surface area has a direct correlation in the amount of tufa precipitation. Thus, it is necessary to conduct a study on the chemical and physical dedolomitization of RPCC aggregate. It is the view of the research team that the recommendations of such study may enable all concrete to be recycled (irrespective of the initial calcium and magnesium content) in future, with new specifications.

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Appendix A

**PORTLAND CEMENT CONCRETE PROJECTS BY COUNTY NAME, MILE MARKER,
FINE AGGREGATE SUPPLIER AND PAVING COMPANY**

TABLE A.1

**PORTLAND CEMENT CONCRETE PROJECTS BY COUNTY NAME, MILE MARKER, FINE
AGGREGATE SUPPLIER AND PAVING COMPANY**

Section A. PROJECTS SELECTED FROM I-70

ODOT Sample #	County Name	Mile Marker	Project #	Designated as Sample # for Research	Fine Aggregate Supplier	Paving Company
1	Preble	0-1.3	784 -60	I-70#1	Am. Agg. Corp Richmond, IN	Fischer Construction Company
2	Preble	9.46-10.44	733 -62	I-70#2	Am. Agg. Corp Richmond, IN	E. K. Bridge Company
3	Montgomery	2.73-3.51	755 -62	I-70#3	Am. Agg. Corp Dayton, OH	Pierce Construction Company
4	Montgomery	6.50-7.35	112 -58	I-70#4	Am. Agg. Corp Dayton, OH	Fischer Construction Company
5	Montgomery	11.19-12.31	490-56	I-70#5	Fenton Construction Company, OH	Fischer Construction Company
6	Montgomery	12.31-13.33	490 -56	I-70#6	Fenton Construction Company, Troy, OH	Fischer Construction Company
7	Montgomery	13.33-14.17	490 -56	I-70#7	Fenton Construction Company, Troy, OH	D. R. Smalley and Sons
8	Franklin	14.65-15.48	21 -64	I-70#8	Am Agg Corp, Frank Road, Columbus, OH	Great Lakes Construction Company
9	Franklin	15.5-16.75	136 -64	I-70#9	Am Agg Corp, Frank Road, Columbus, OH	Fvelotta and Sons

10	Franklin	18.21-19.64	273 -64	I-70#10	Am Agg Corp, Lockbourne, OH	Chapin and Chapin
11	Franklin	19.64-22.24	598 -64	I-70#11	Am Agg Corp, Frank Road, Columbus, OH	Chapin and Chapin
12	Guernsey	20.75-23.50	276 -65	I-70#12	Spring Construction Company, Newcomerstown, OH	V. N. Holderman and Sons
13	Guernsey	25.75-26.75	335 -63	I-70#13	Stocker Sa and Gr. Comp, Port Washington, OH	Fischer Construction Company
14	Guernsey	27.0-27.75	244 -64	I-70#14	Stocker Sa and Gr. Comp, Port Washington, OH	Fischer Construction Company
15	Belmont	0.95-3.91	597 -64	I-70#15	Stocker Sa and Gr. Comp, Port Washington, OH.	Fischer Construction Company
16	Belmont	5.09-7.66	529 -66	I-70#16	Edgar Spr Inc, Medrale.	Fischer Construction Company
17	Belmont	15.72-16.74	204 -63	I-70#17	Blaney Sa and Gr. Comp, Clarington, OH.	Fischer Construction Company

Section B. PROJECTS SELECTED FROM I-71.

ODOT Sample #	County Name	Mile Marker	Project #	Designated as Sample # for Research	Fine Aggregate Supplier	Paving Company
1	Hamilton	11.51-13.07	278 -65	I-71#1	Queen City Gr., Camp Denison	Foley Construction Company
2	Hamilton	13.07-15.24	612 -64	I-71#2	Queen City Gr., Camp Denison	Desolvo Construction Company
3	Warren	14.69-14.99	734 -62	I-71#3	Morrow S and Gr. Co, Morrow, OH.	Fischer Construction Company
4	Clinton	9.11-12.12	748 -62	I-71#4	Moraine Materials, Moraine, OH.	Rhoten Construction Company
5	Clinton	12.12-12.68	748 -62	I-71#5	Moraine Materials, Moraine, OH.	Rhoten Construction Company
6	Cuyahoga	0.00-2.61	357 -63	I-71#6	Slag Company, Crystal Spring, OH	Great Lakes Construction Company
7	Cuyahoga	2.61-3.42	357 -63	I-71#7	Slag Company, Crystal Spring, OH	Great Lakes Construction Company
8	Cuyahoga	17.19-17.83	274 -65	I-71#8	Erie Sa and Gr., Pelee Isl, Ontario.	Great Lakes Construction Company
9	Cuyahoga	17.83-18.54	79 -65	I-71#9	Na As and Materials, Pelee Isl. Ontario.	V. N. Holdermann and Sons

Section C. PROJECTS SELECTED FROM I-75.

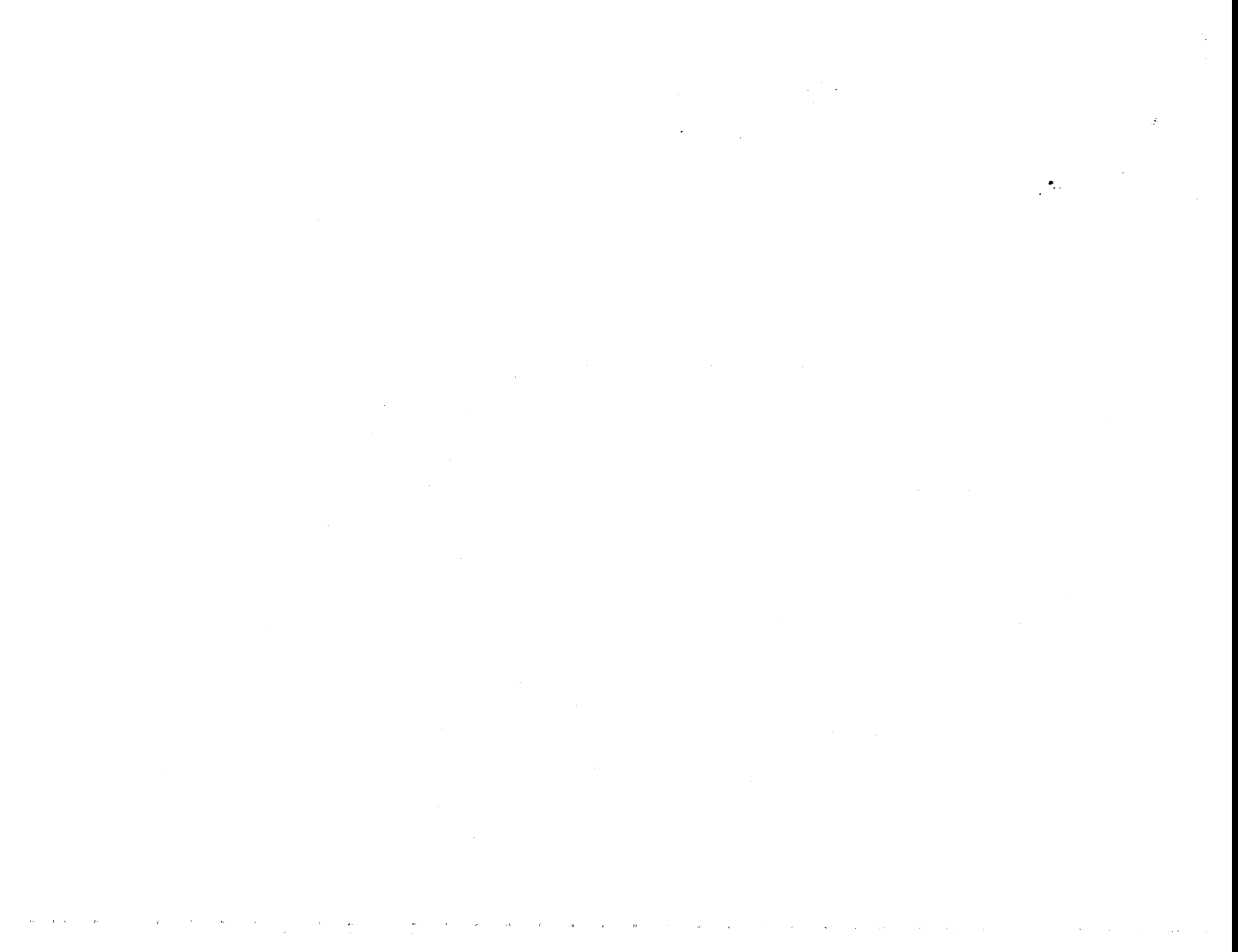
ODOT Sample #	County Name	Mile Marker	Project #	Designated as Sample # for Research	Fine Aggregate Supplier	Paving Company
1	Hamilton	1.00-1.72	766 -60	I-75#1	Queen City Gr. Co Cleves, OH	Foley Construction Company
2	Hamilton	6.64-7.74	362 -56	I-75#2	Ohio Gr. Co, Newtown.	Foley Construction Company
3	Montgomery	0.49-1.31	625 -58	I-75#3	Southern Ohio Gr. Co, Franklin, OH.	Fischer Construction Company
4	Montgomery	9.43-10.65	51 -64	I-75#4	Am Agg Corp, Dayton, OH.	W. L. Johnson Construction Company
5	Sheby	4.85-9.48	83 -58	I-75#5	Ernst Gravel Co, Pigua, OH.	G.W. Lathrop and Sons
6	Wood	26.86-30.62	310 -65	I-75#6	Erie Sand and Gr. Co, Sandusky, OH.	Pierce Construction Company
7	Allen	6.12-9.07	555 -55	I-75#7	C.E. Duff, Westminster, OH.	V.N. Holderman Construction Company

Section D. PROJECTS SELECTED FROM I-77.

ODOT Sample #	County Name	Mile Marker	Project #	Designated as Sample # for Research	Fine Aggregate Supplier	Paving Company
1	Noble	10.88-13.82	732 -66	I-77#1	Muskingum River Gr., Duncan Falls, OH	Shelly and Sands Corporation
2	Noble	16.28-18.92	591- 65	I-77#2	Stocker Sa and Gr., Port Washington, OH.	Construction and Materials Company
3	Stark	12.36-16.66	727 -61	I-77#3	Canton Agg, Plt 2, N. Canton.	Lane Construction Company
4	Summit	24.10-28.27	598 -61	I-77#4	Wilson Sand Company, Upper Sandusky, OH.	J. Rublin, W.E. Ringwald and Sons
5	Cuyahoga	2.04-4.07	653 -66	I-77#5	Jefferson Materials, Streetsboro, OH.	M.F. Velotta and Sons
6	Cuyahoga	4.07-6.43	418 -67	I-77#6	Standard Slag Co., Shalersville, OH.	Horvitz Company
7	Cuyahoga	12.10-13.25	447 -47	I-77#7	J. P. Loomis, Akron, OH.	Horvitz Company
8	Cuyahoga	14.16-14.50	321 -63	I-77#8	Erie S and Gr. Pelee Island.	Horvitz Company

Section E. PROJECTS SELECTED FROM I-90.

ODOT Sample #	County Name	Mile Marker	Project #	Designated as Sample # for Research	Fine Aggregate Supplier	Paving Company
1	Lorain	12.00-13.01	524 -65	I-90#1	Lorain-Elyria Sa and Gr., Lorain, OH.	Chopin and Chopin
2	Lorain	13.01-17.22	173 -66	I-90#2	Lorain-Elyria Sa and Gr., Lorain, OH.	H. Miller and Mosser Construction
3	Cuyahoga	13.81-14.94	183 -65	I-90#3	Nat. Sa and Materials, Pelee Islands, Ontario.	Horovitz Company
4	Cuyahoga	14.94-15.31	183 -65	I-90#4	Nat. Sa and Materials, Pelee Islands, Ontario	Horovitz Company
5	Cuyahoga	8.27-9.91	572 -59	I-90#5	Sidley Gr.	Horovitz Company
6	Cuyahoga	13.68-14.97	148 -61	I-90#6	Standard Sl. Co, Crystal Spring, OH.	Horovitz Company



Appendix B

**TG-DTA EXPERIMENTAL CONDITIONS, METHODS OF CALCULATION,
TOGETHER WITH THE TG-DTA PLOTS FOR ALL THE RPCC AGGREGATES
EXAMINED.**

Instrument:

Simultaneous TG-DTA Instrument (Model 2960, TA Instruments).

Apparatus:

1. 2 Platinum Crucibles.
2. Flow meter.
3. 2 Gas Drying Tubes (Drierite).
4. Gas flow Controlling Device.
5. N₂ Gas Cylinder.
6. CO₂ Gas Cylinder.

Experimental Conditions:

Fine powder for each sample (passed through sieve #200) is used in this experiment.

- Sample size: 25-30 mg.
- Sample Crucible: 110 μ L platinum crucible.
- Reference crucible: 110 μ L platinum crucible (empty).
- Heating rate: 10 degrees per minute.
- Temperature range:
 - a. Ambient to 1000 degrees Celcius (For dry Nitrogen).
 - b. Ambient to 1100 degrees Celcius (For dry Carbon Dioxide).
- Atmosphere:
 - a. Dry N₂.
 - b. Dry CO₂.

Calculation:

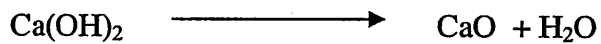
Molecular weights of $\text{CO}_2 = 44.01$ $\text{Ca(OH)}_2 = 74.09$ $\text{CaCO}_3 = 100.09$ $\text{MgCO}_3 = 84.31$
 $\text{H}_2\text{O} = 18.02$

ML_{dh} = Mass loss due to dehydration.

ML_{dx} = Mass loss due to dehydroxylation.

ML_{dc} = Mass loss due to decarbonation.

For Dehydroxylation:



Eqn 1.

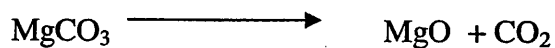
1 mole H_2O loss = 1 mole Ca(OH)_2 present.

$$\frac{\% \text{ML}_{\text{H}_2\text{O}}}{18.02} = \frac{\% \text{ML}_{\text{Ca(OH)}_2}}{74.09}$$

Therefore,

$$\% \text{ML}_{\text{Ca(OH)}_2} = 4.11 \% \text{ML}_{\text{H}_2\text{O}}$$

For Decarbonation:



Eqn 2.

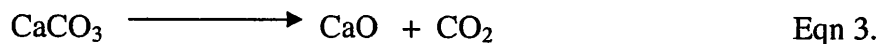
1 mole CO_2 loss = 1 mole MgCO_3 present.

$$\frac{\% \text{ML}_{\text{CO}_2}}{44.01} = \frac{\% \text{ML}_{\text{MgCO}_3}}{84.31}$$

Therefore,

$$\% \text{ML}_{\text{MgCO}_3} = 1.92 \% \text{ML}_{\text{CO}_2}$$

For Decarbonation of CaCO₃:



1 mole CO₂ loss = 1 mole CaCO₃ present.

$$\frac{\% \text{ML}_{\text{CO}_2}}{44.01} = \frac{\% \text{ML}_{\text{CaCO}_3}}{100.09}$$

Therefore,

$$\% \text{ML}_{\text{CaCO}_3} = 2.27 \% \text{ML}_{\text{CaCO}_3}$$

The above calculations for MgCO₃ and CaCO₃ yield % mass loss for such compounds as total estimations. Powder x-ray diffraction (XRD) patterns reveal that Calcite (CaCO₃), Dolomite (CaCO₃ MgCO₃), Quartz (SiO₂), Portlandite (Ca(OH)₂), Lime (CaO), Gypsum (CaSO₄) along with miniscule amount of many other materials are present in the samples. As a result, the TG-DTA results carried out in the atmosphere of dry CO₂ were recalculated as %Dolomite and as %CaCO₃ by assuming that all MgCO₃ existed in the form of dolomite.

Dolomite has a formula MgCO₃ CaCO₃ which is an equimolar compound of magnesium carbonate and calcium carbonate.

To determine the amount of CaCO₃ required for Dolomite

84.31 grams of MgCO₃ requires 100.09 grams of CaCO₃ in dolomite.

X grams of MgCO₃ requires 1.187X grams of CaCO₃ in dolomite.

Therefore, % Dolomite in the sample = %MgCO₃ + CaCO₃

$$= \%X + \%1.187X.$$

and %CaCO₃ remaining = Total Estimated CaCO₃ - 1.187 X.

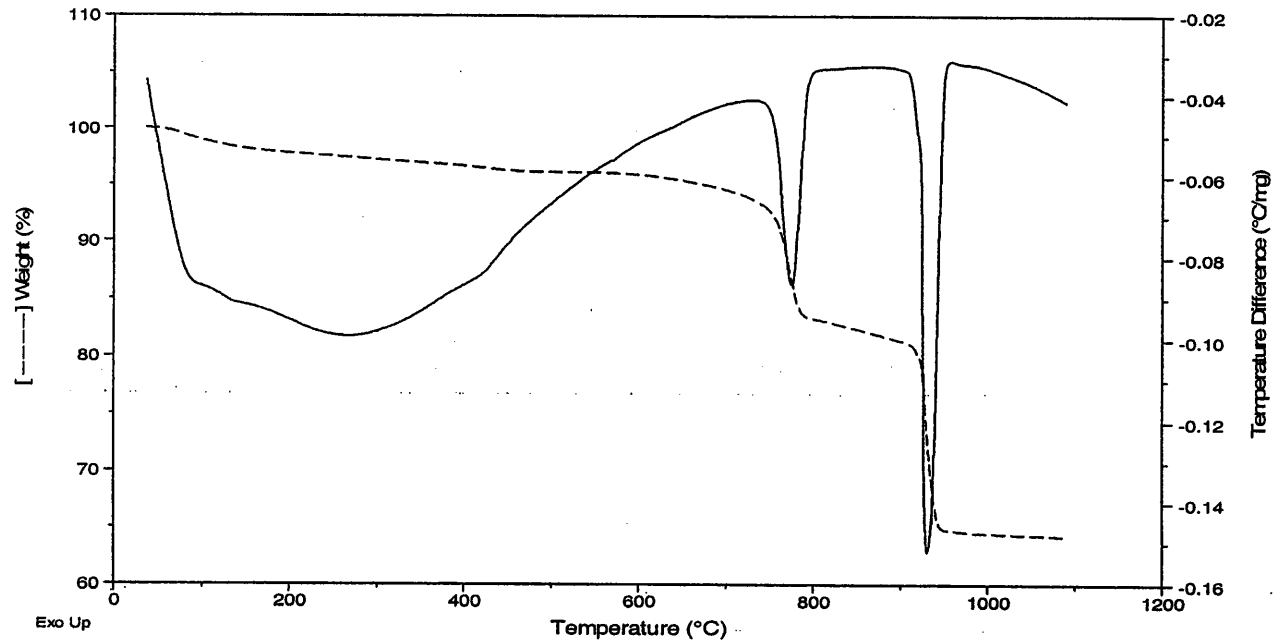
Appendix B, Section 1

The TG-DTA Plots for all the RPCC Aggregates tested in CO₂ Atmosphere

Sample: I70 # 1
Method: 10°C/MIN TO 1100°C
Comment: Dry CO2, 100 mL/min

TGA-DTA

File: C:\ODOT\I70-1.c01
Operator: Supaporn

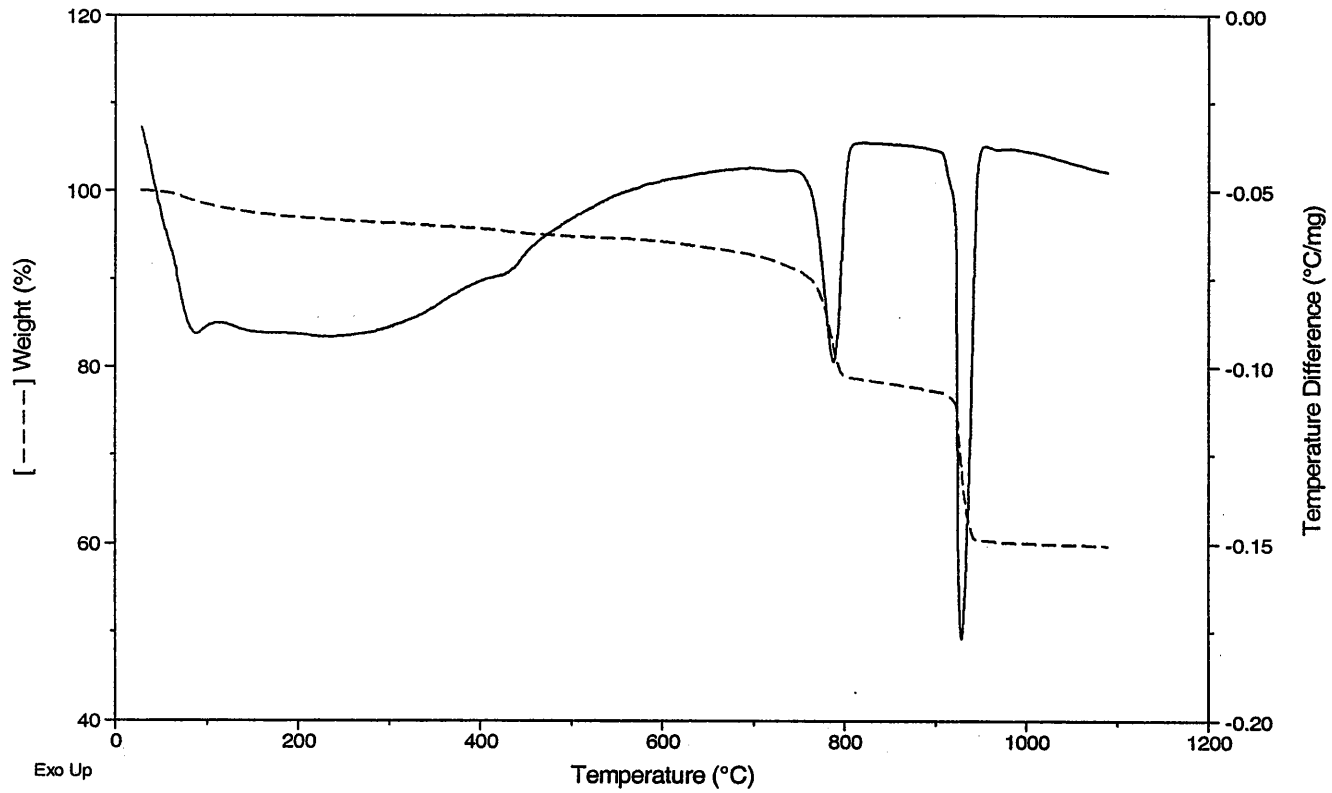


Sample: I70 # 2
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-2.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

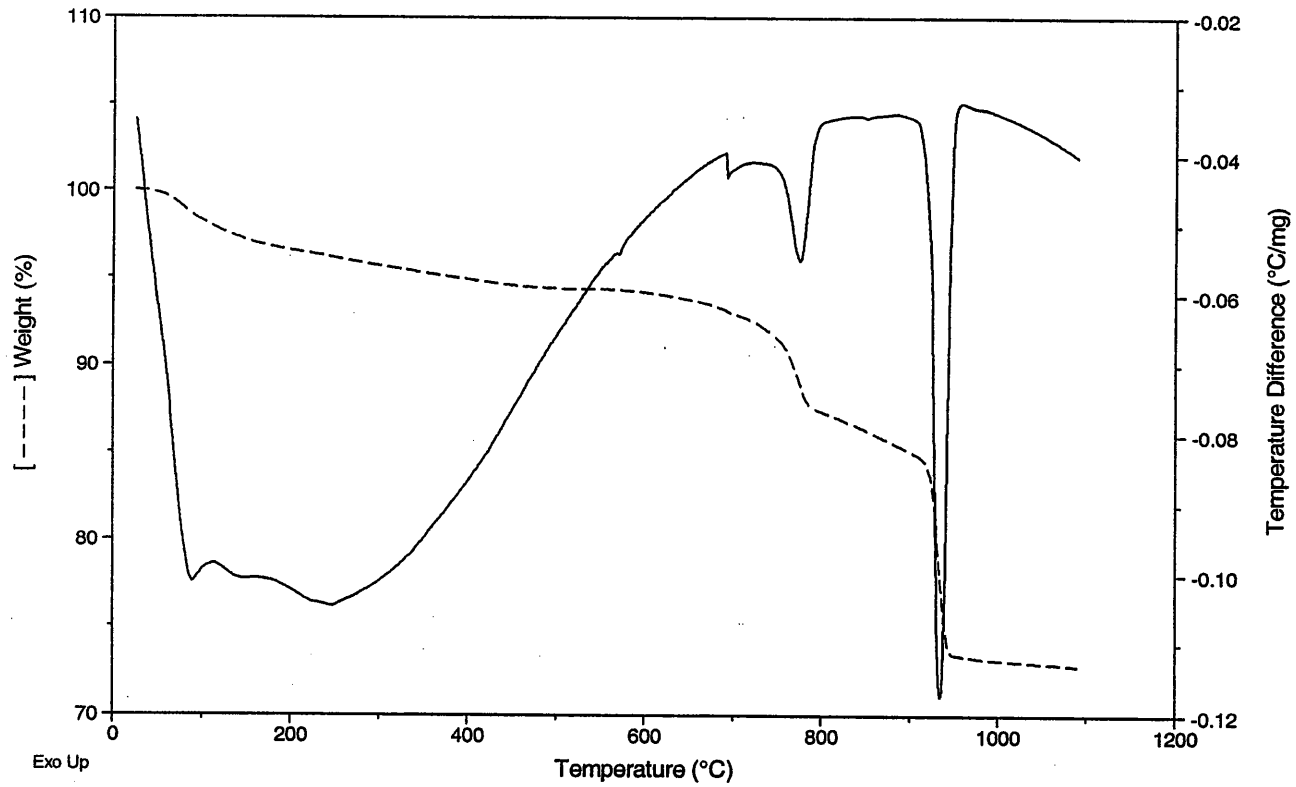


Sample: I 70 # 3
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-3.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

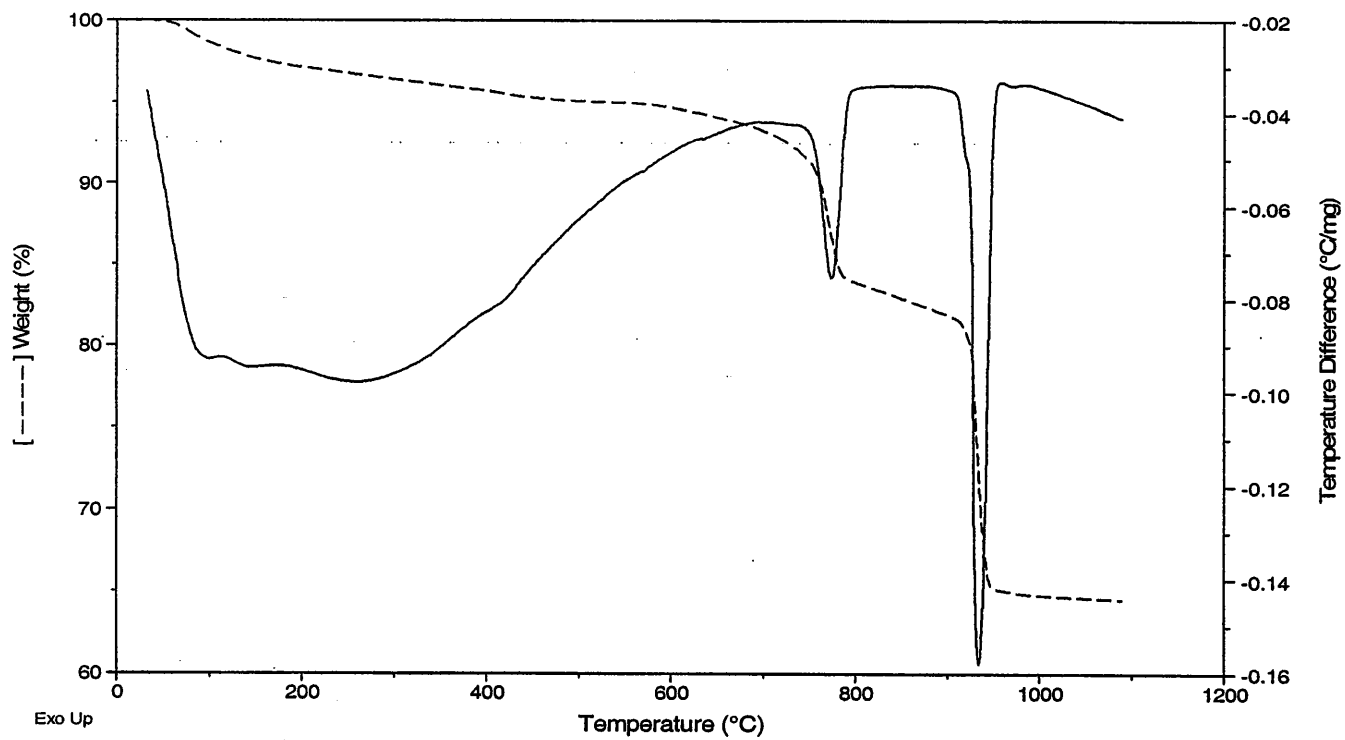


Sample: I 70 # 4
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-4.c01
Operator: Supaporn

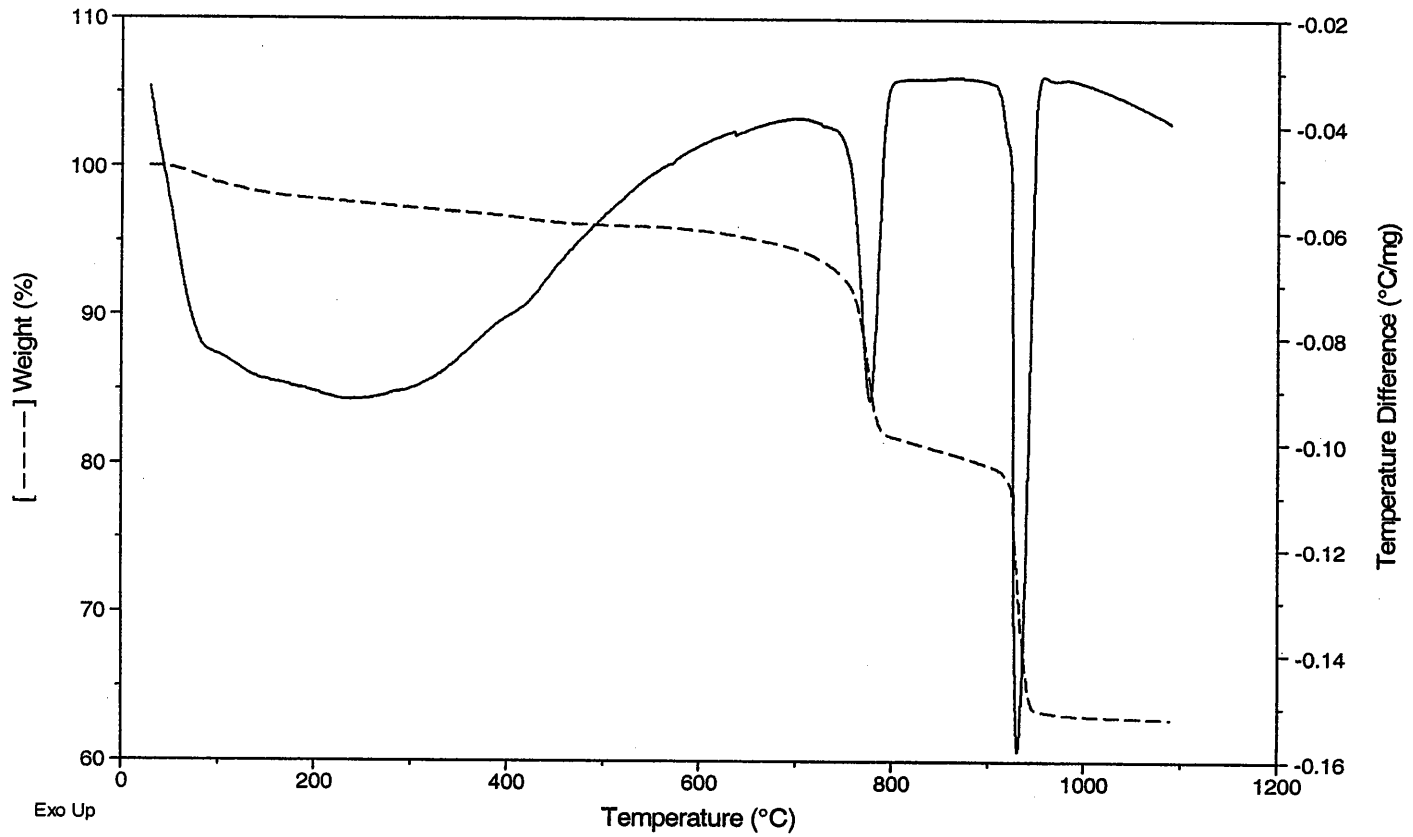
Comment: Dry CO₂, 100 mL/min



Sample: I 70 # 5
Method: 10°C/MIN TO 1100°C
Comment: Dry CO2, 100 mL/min

TGA-DTA

File: C:\ODOT\I70-5.c01
Operator: Supaporn

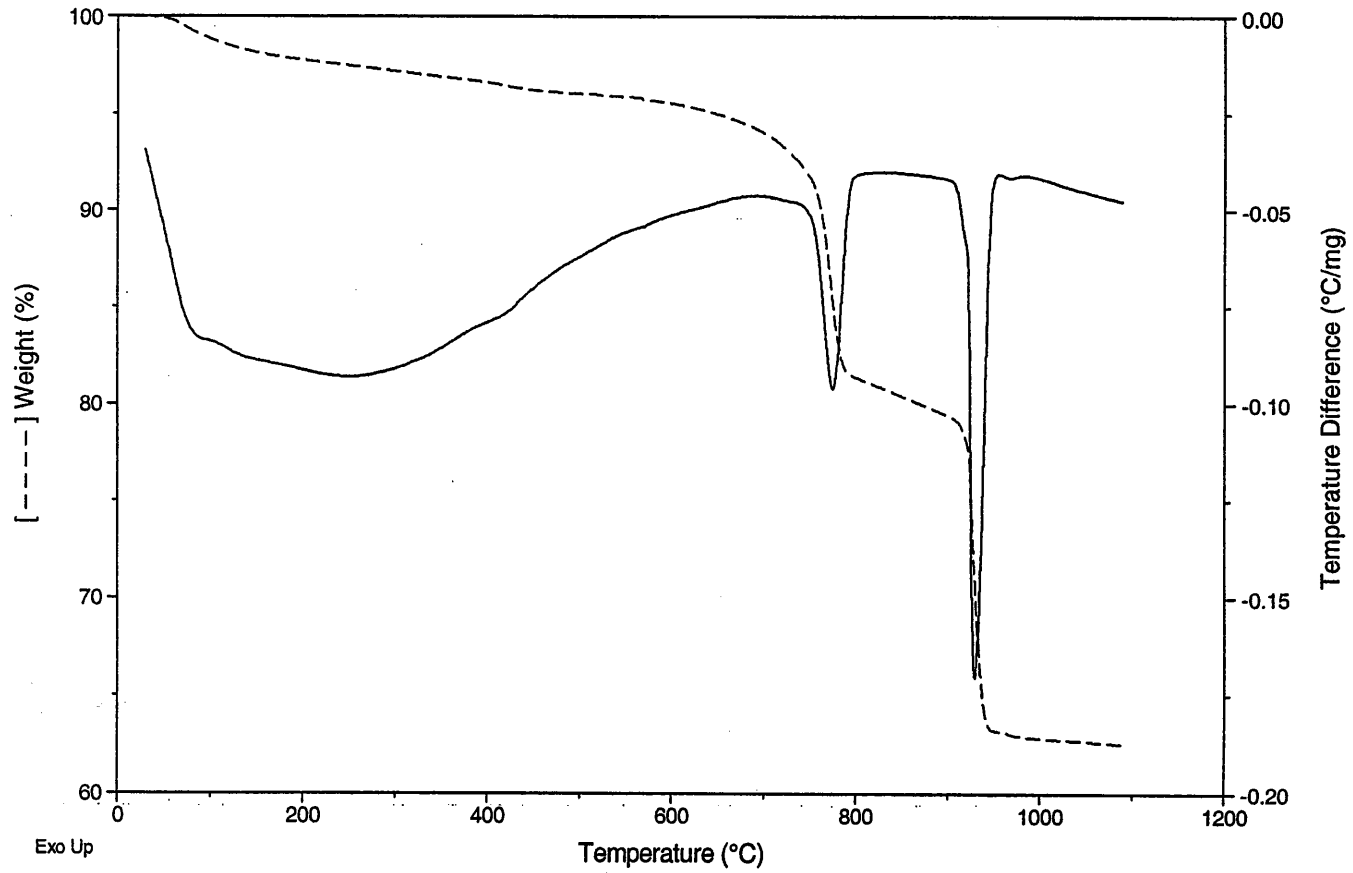


Sample: I70 # 6
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-6.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

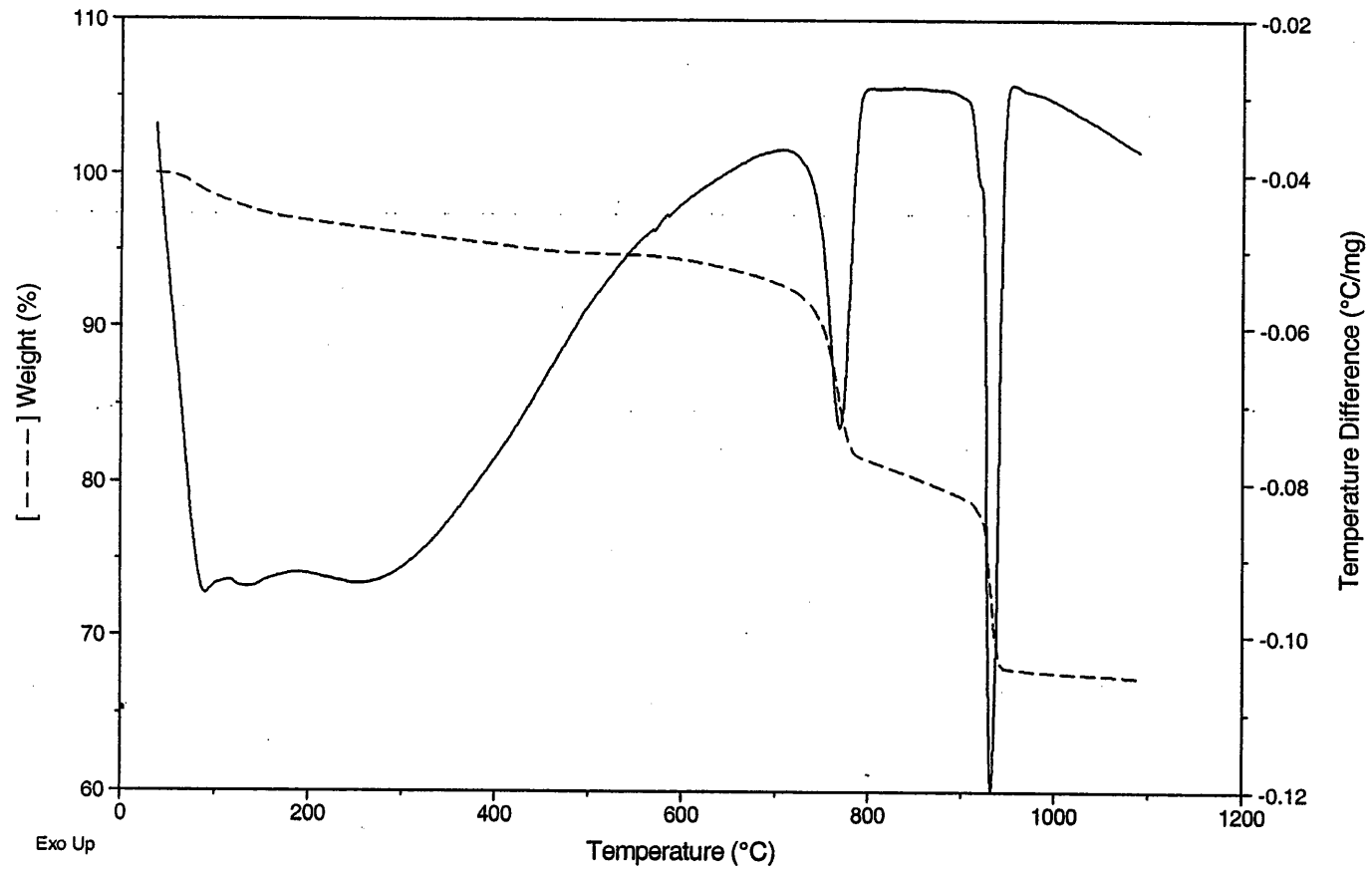


Sample: I70 # 7
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-7.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

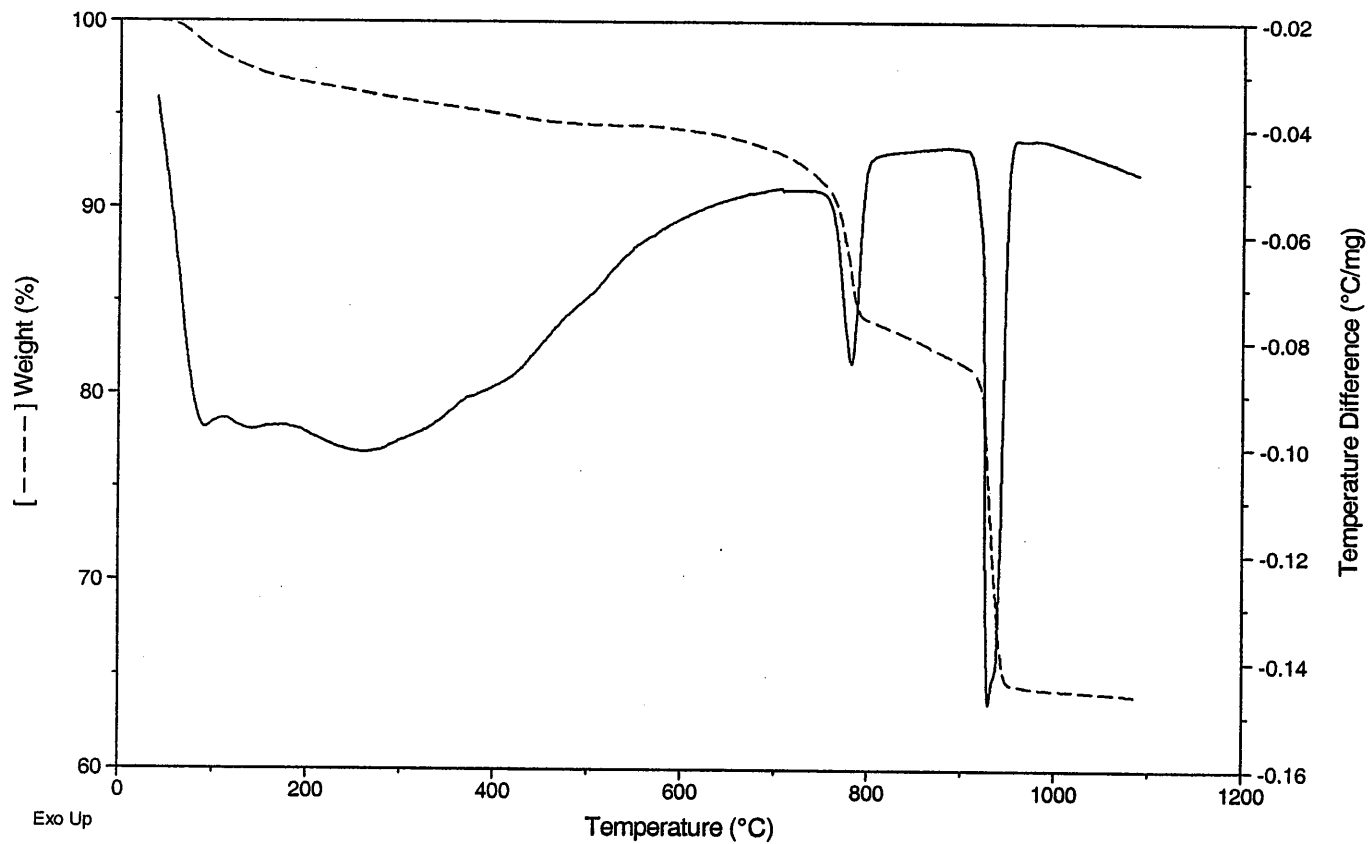


Sample: I70 # 8
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-8.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

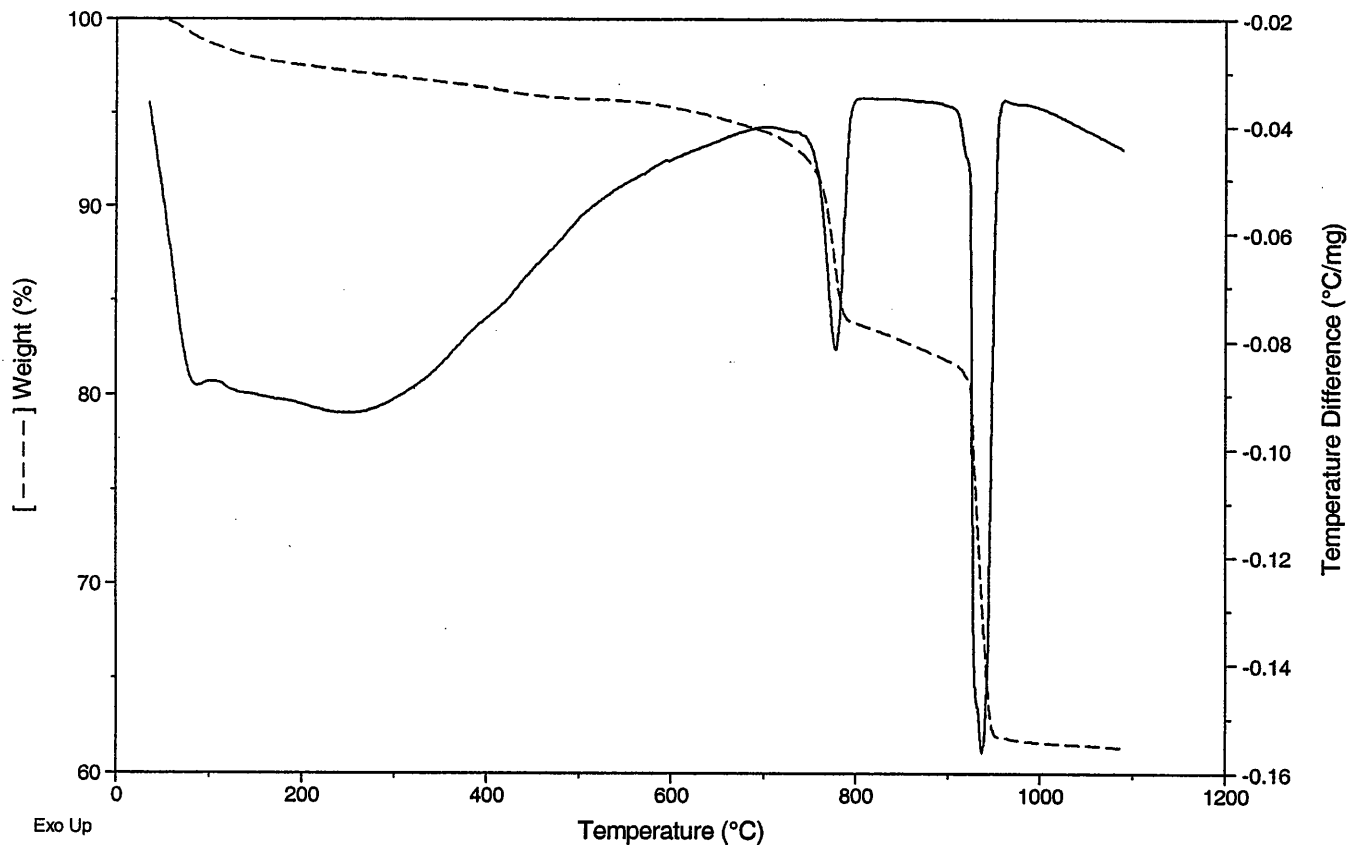


Sample: I70 # 9
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-9.c01
Operator: Supaporn

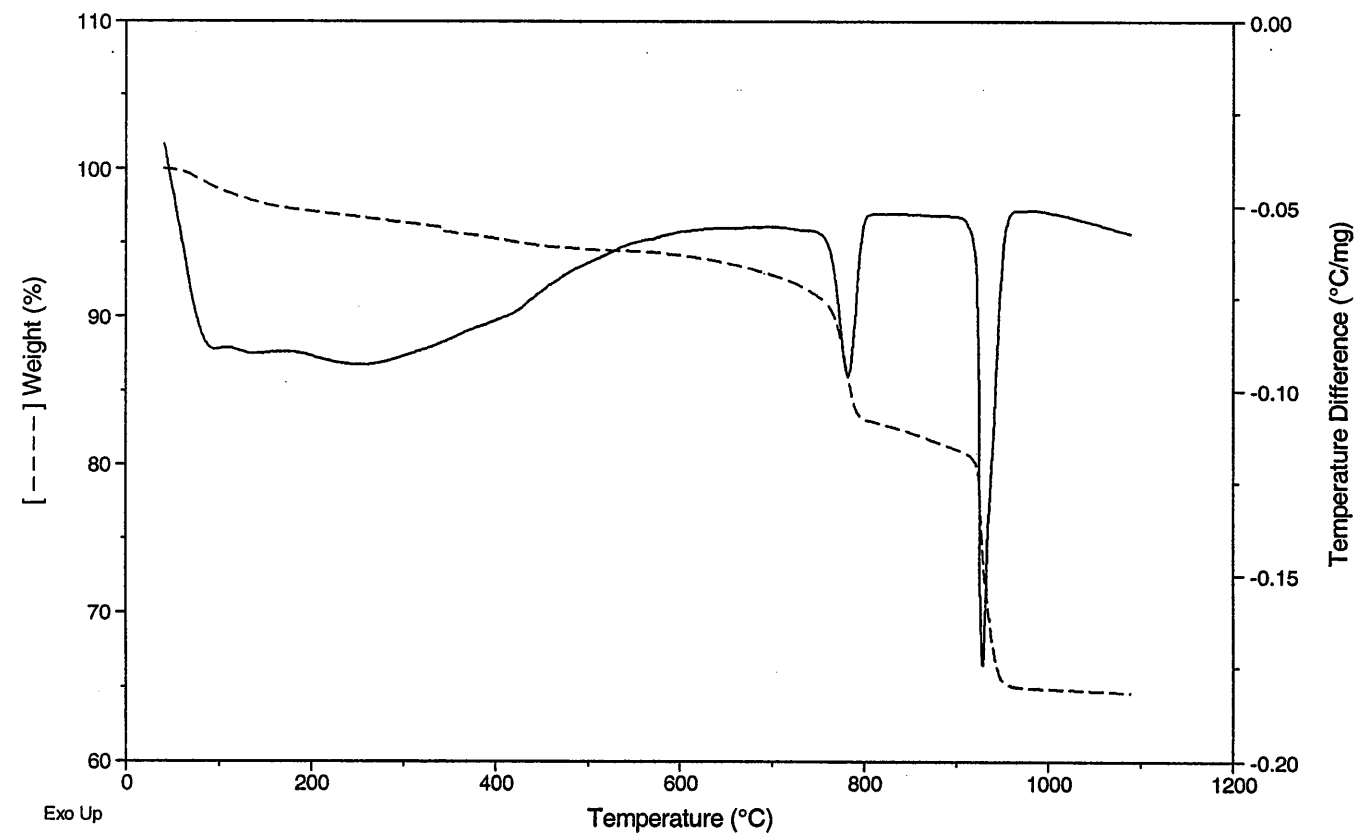
Comment: Dry CO2, 100 mL/min



Sample: I70 # 10
Method: 10°C/MIN TO 1100°C
Comment: Dry CO2 100 mL/min

TGA-DTA

File: C:\ODOT\I70-10.c01
Operator: Supaporn

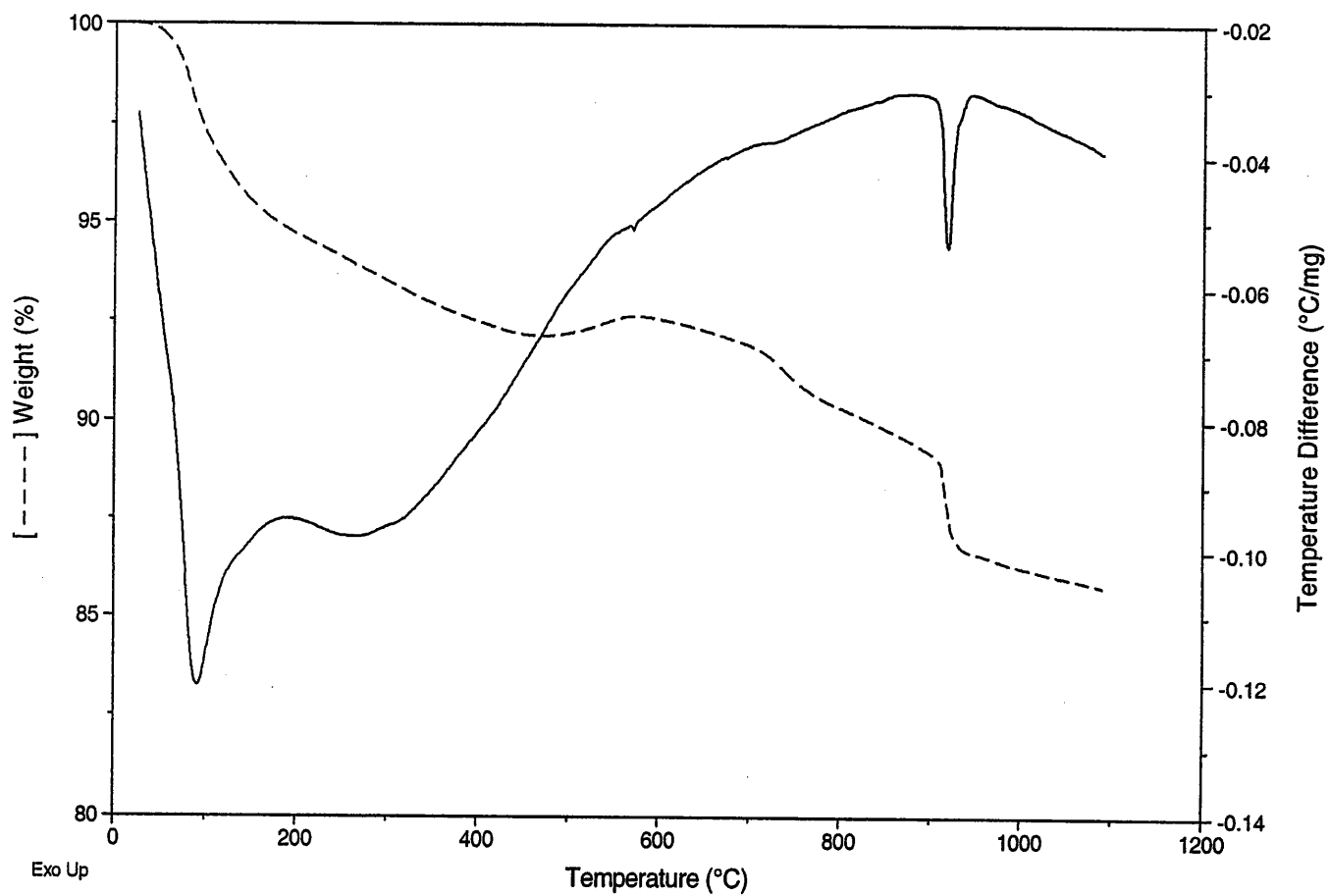


Sample: I70-11
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-11.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

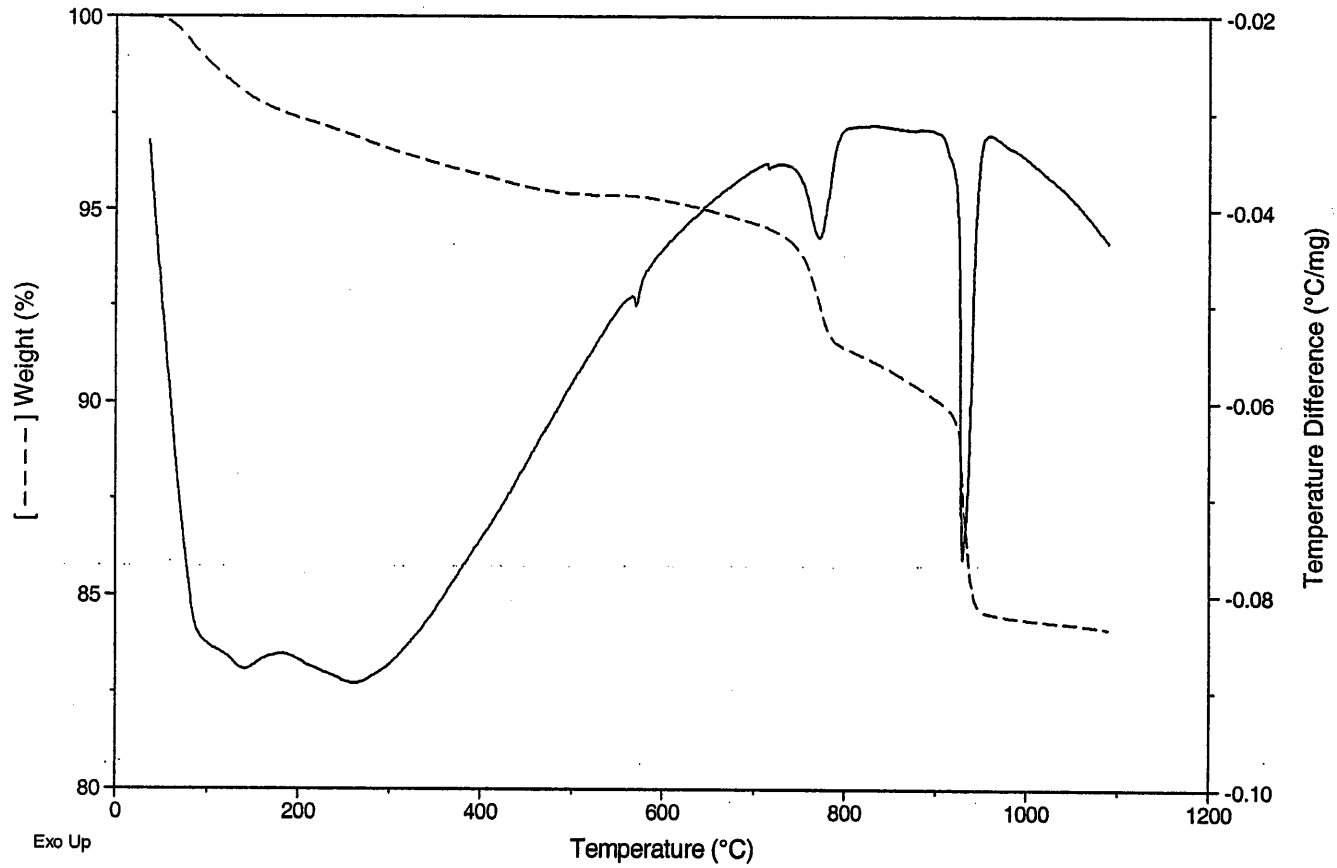


Sample: I70-12
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-12.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

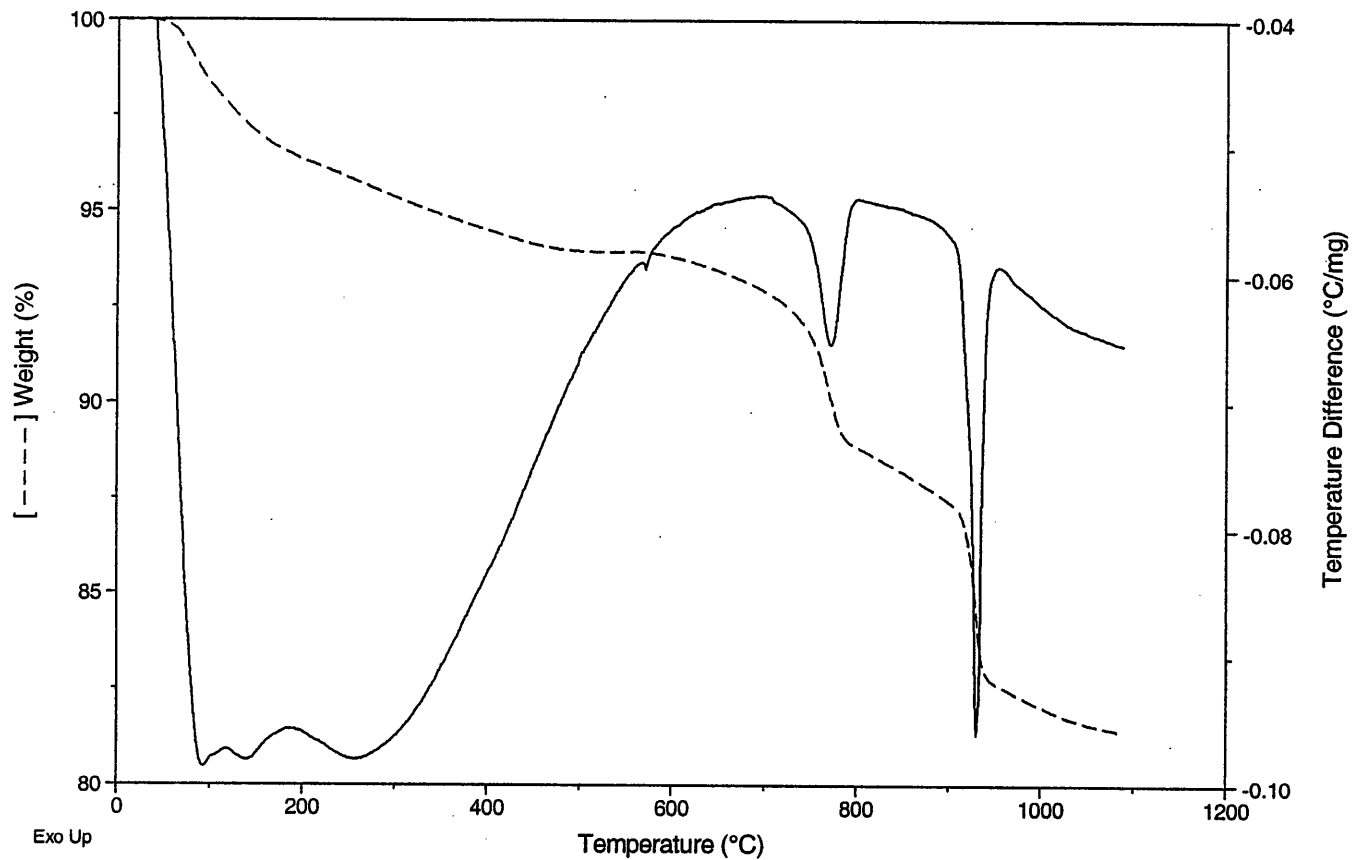


Sample: I70 # 13
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-13.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

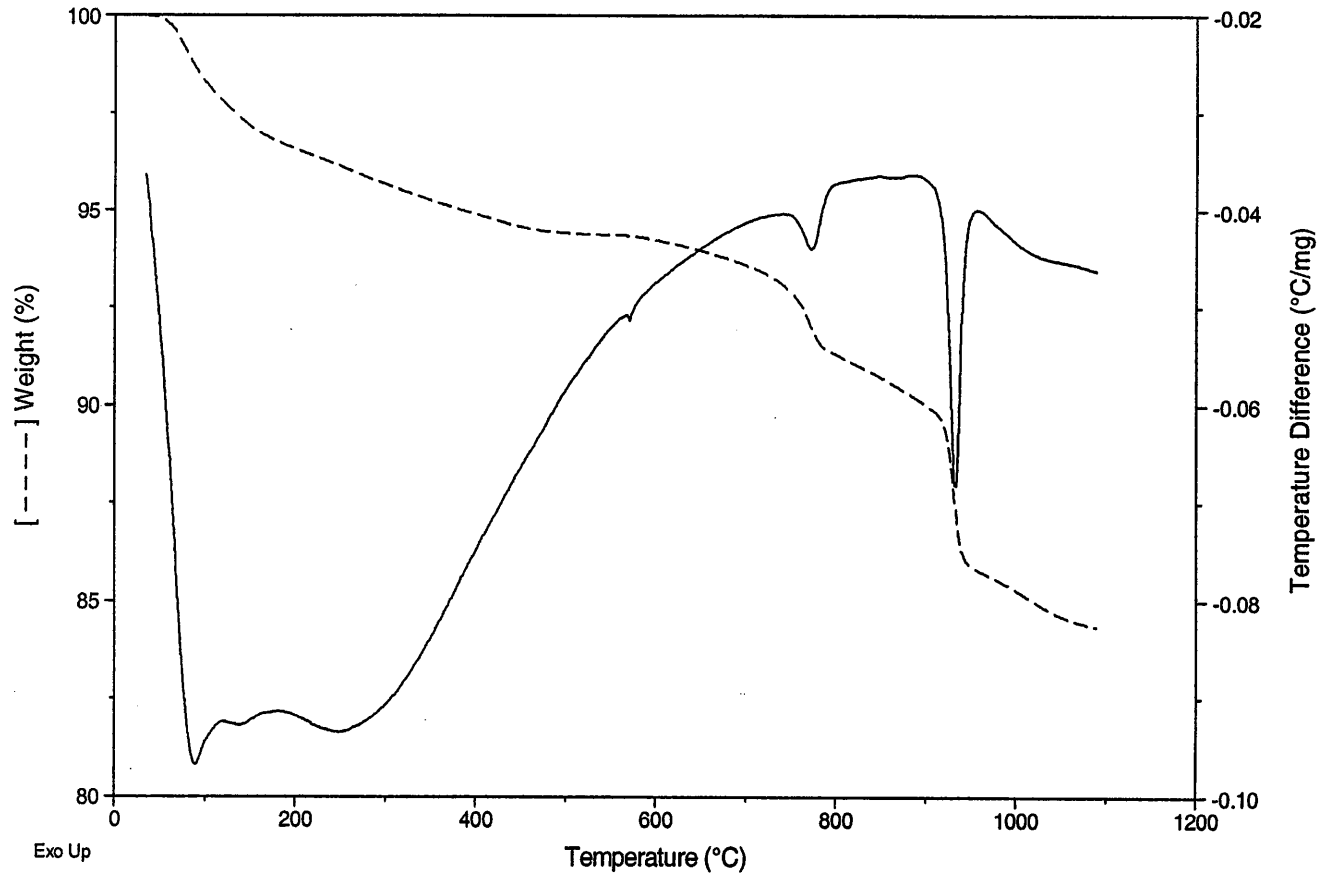


Sample: I70-14
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I70-14.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

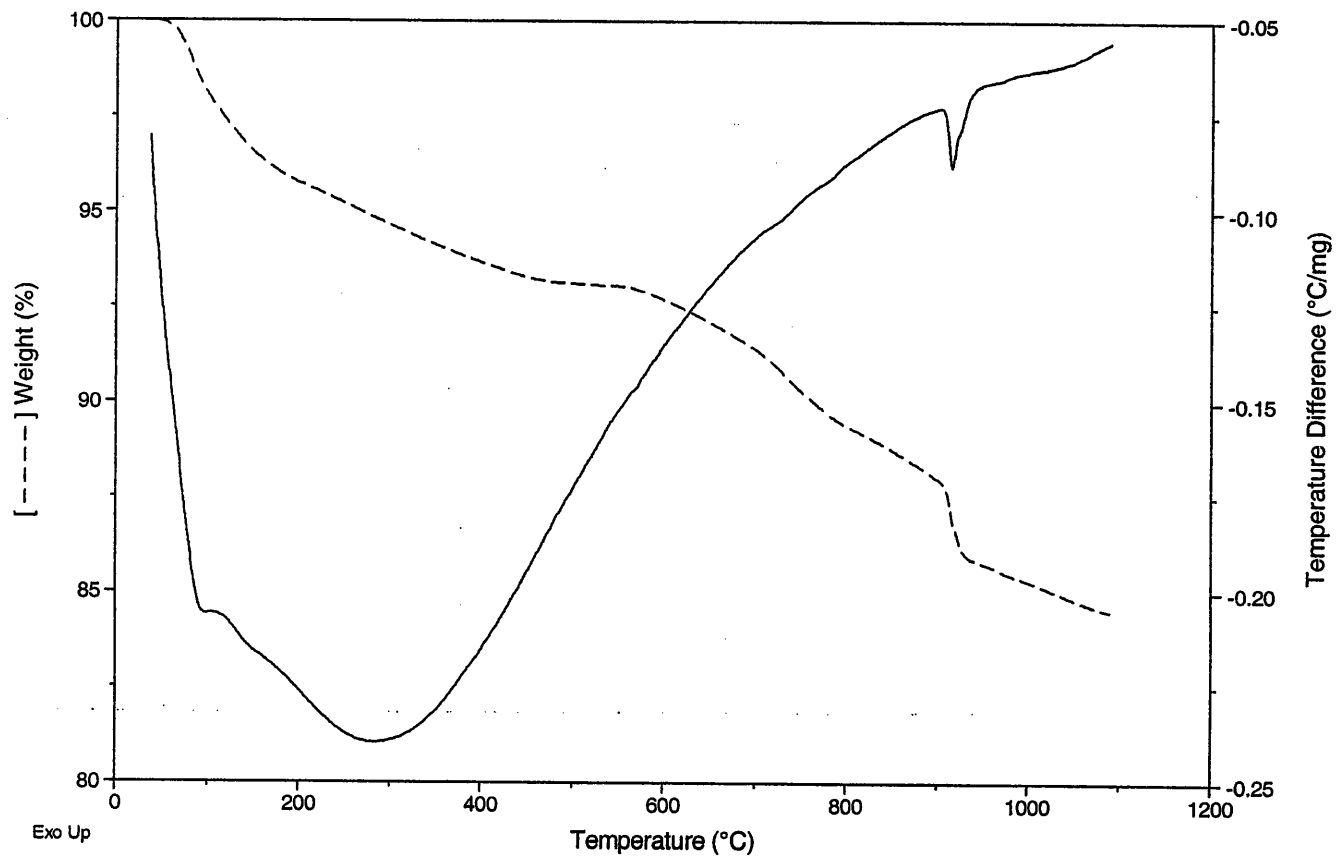


Sample: I70 # 15
Method: 10°C/min to 1100°C

TGA-DTA

File: C:\ODOT\I70-15.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

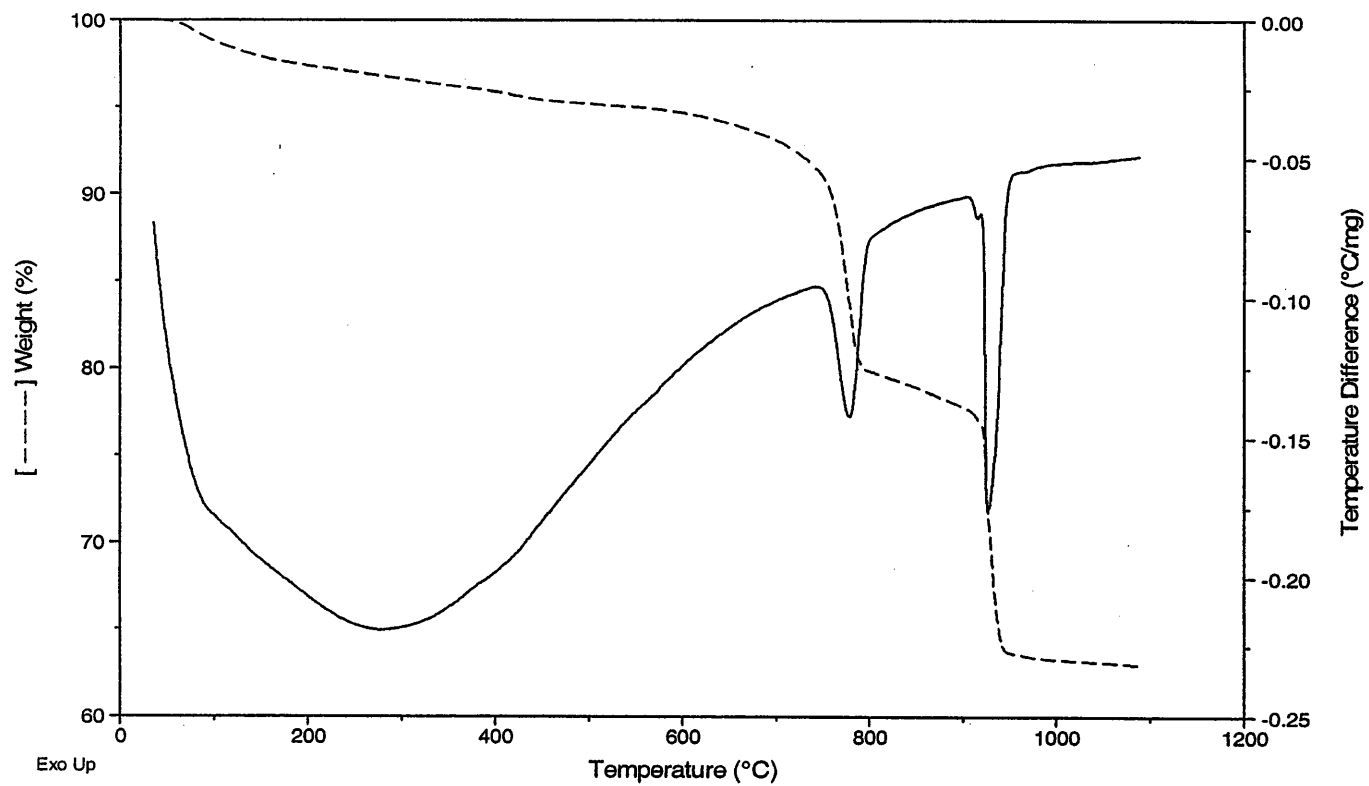


Sample: I70 # 16
Method: 10°C/min to 1100°C

TGA-DTA

File: C:\ODOT\I70-16.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

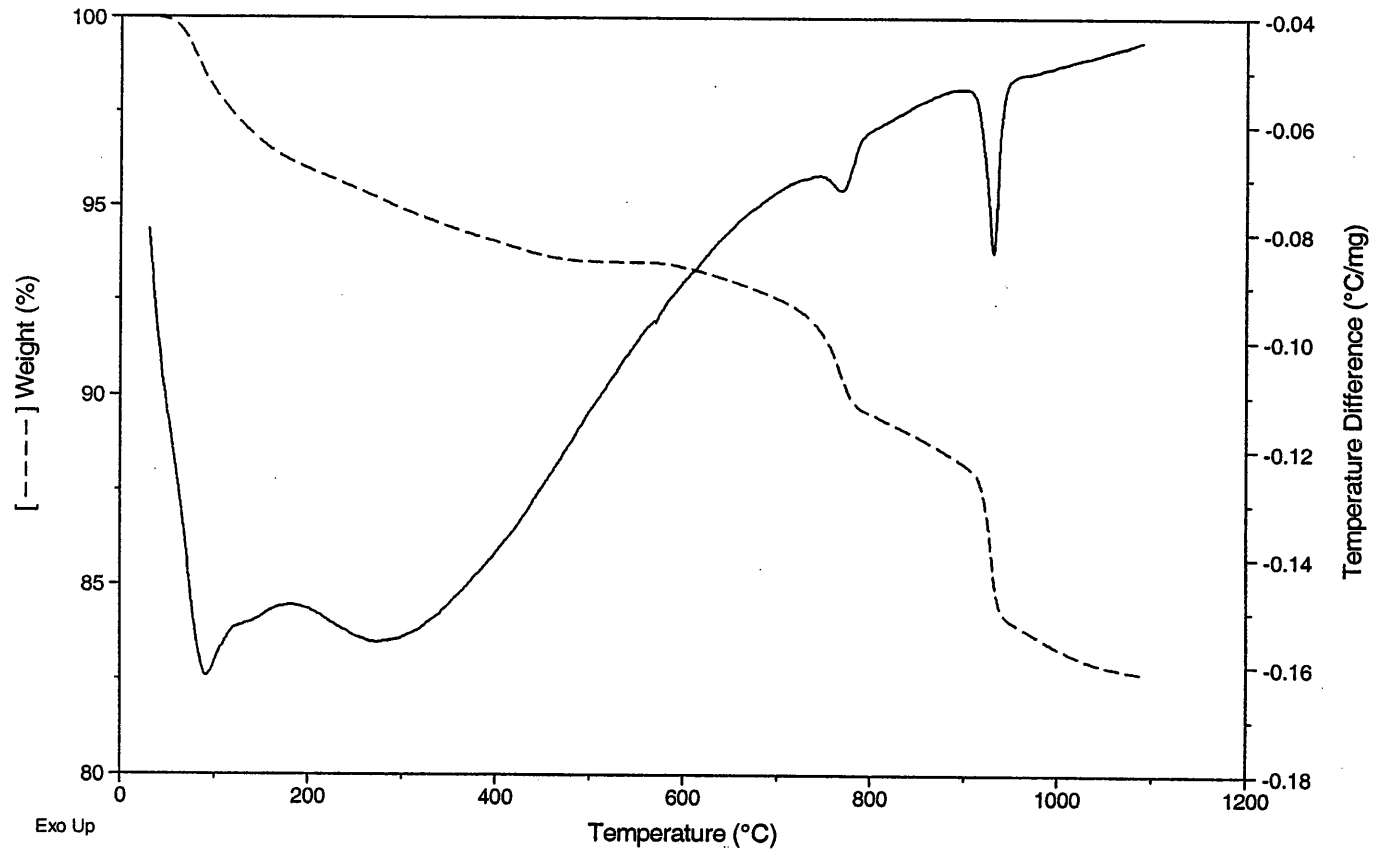


Sample: I 70 # 17
Method: 10°C/min to 1100°C

TGA-DTA

File: C:\ODOT\I70-17.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

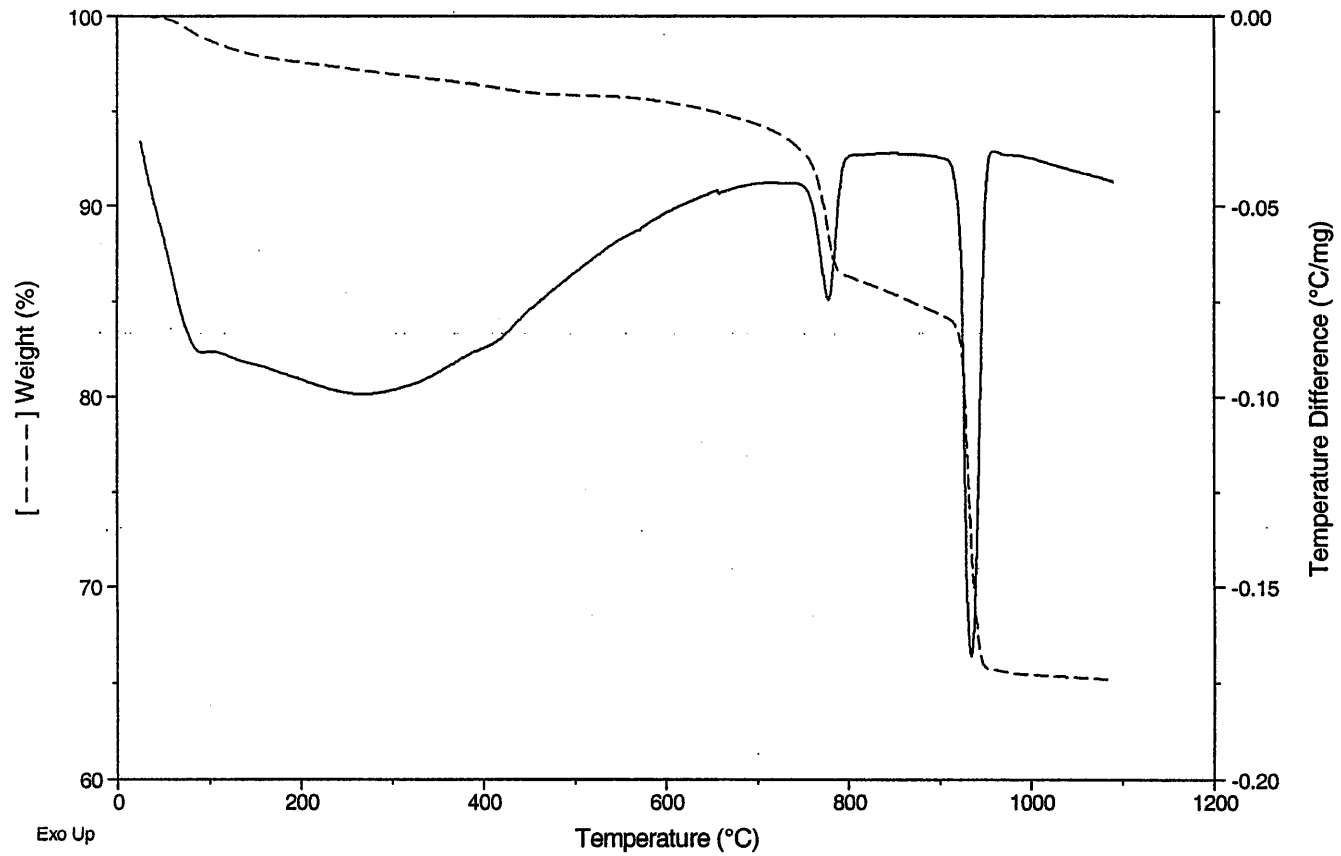


Sample: I71 # 1
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-1.c01
Operator: Supaporn

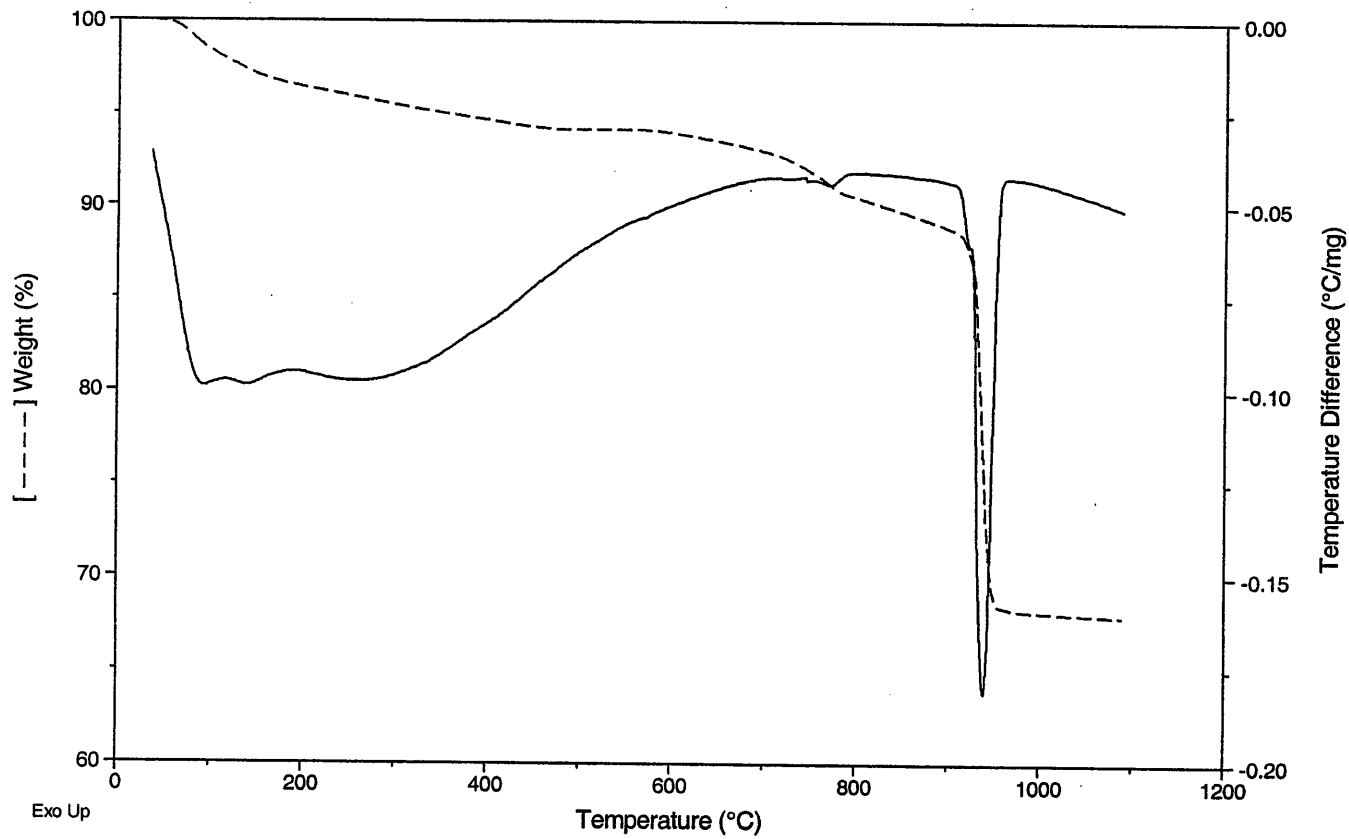
Comment: Dry CO2, 100 mL/min



Sample: I71 # 2
Method: 10°C/MIN TO 1100°C
Comment: Dry CO2, 100 mL/min

TGA-DTA

File: C:\ODOT\I71-2.c01
Operator: Supaporn

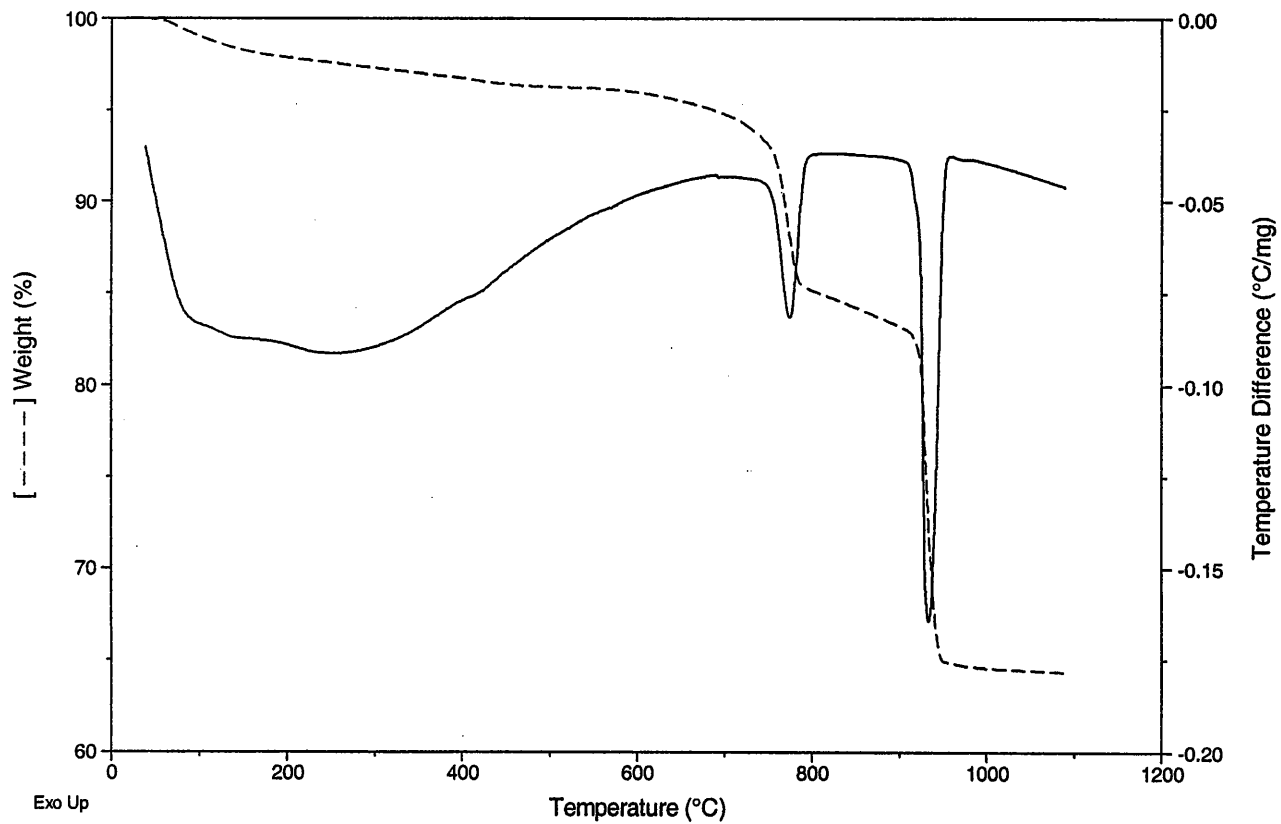


Sample: I71 #3
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-3.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

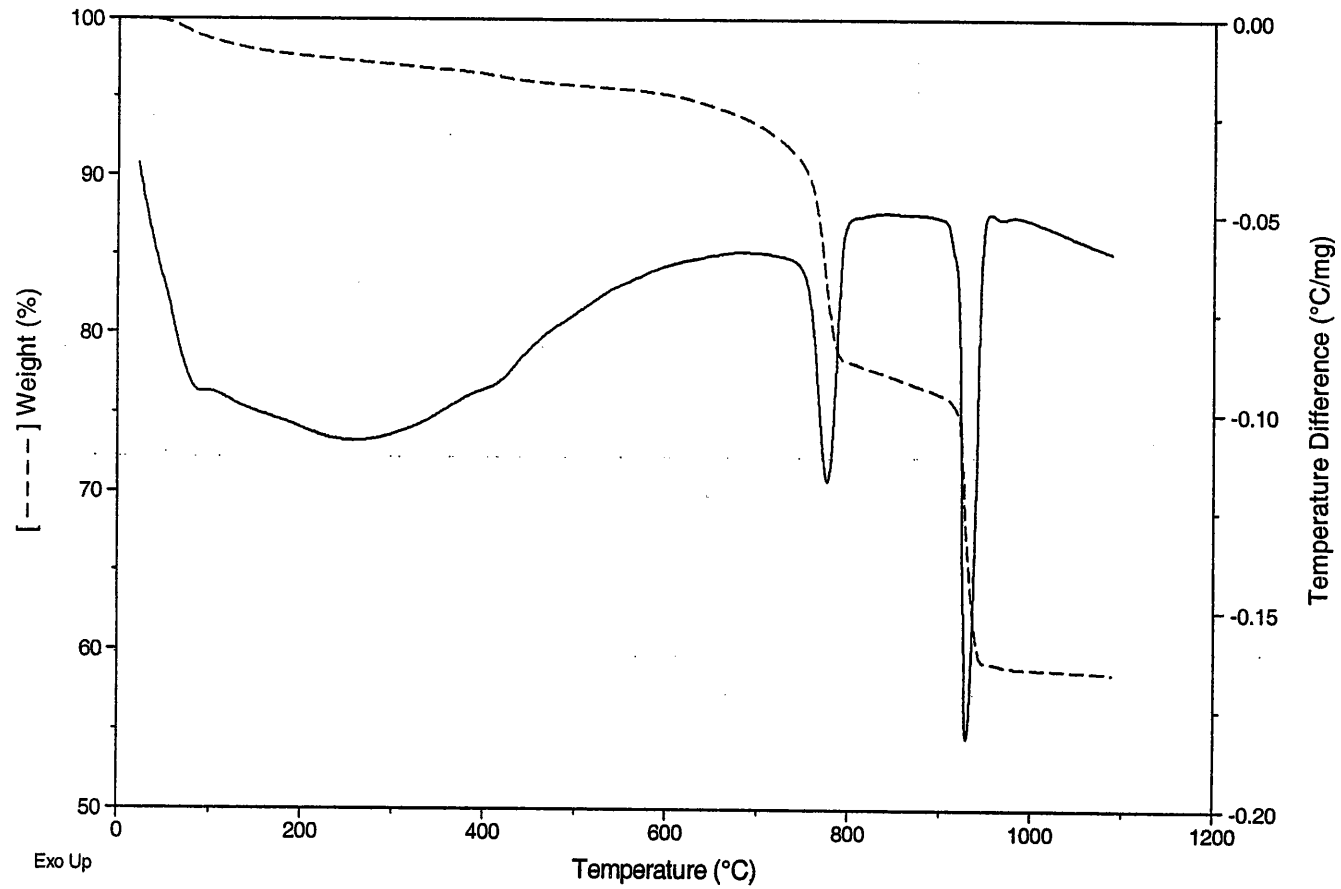


Sample: I71 # 4
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-4.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

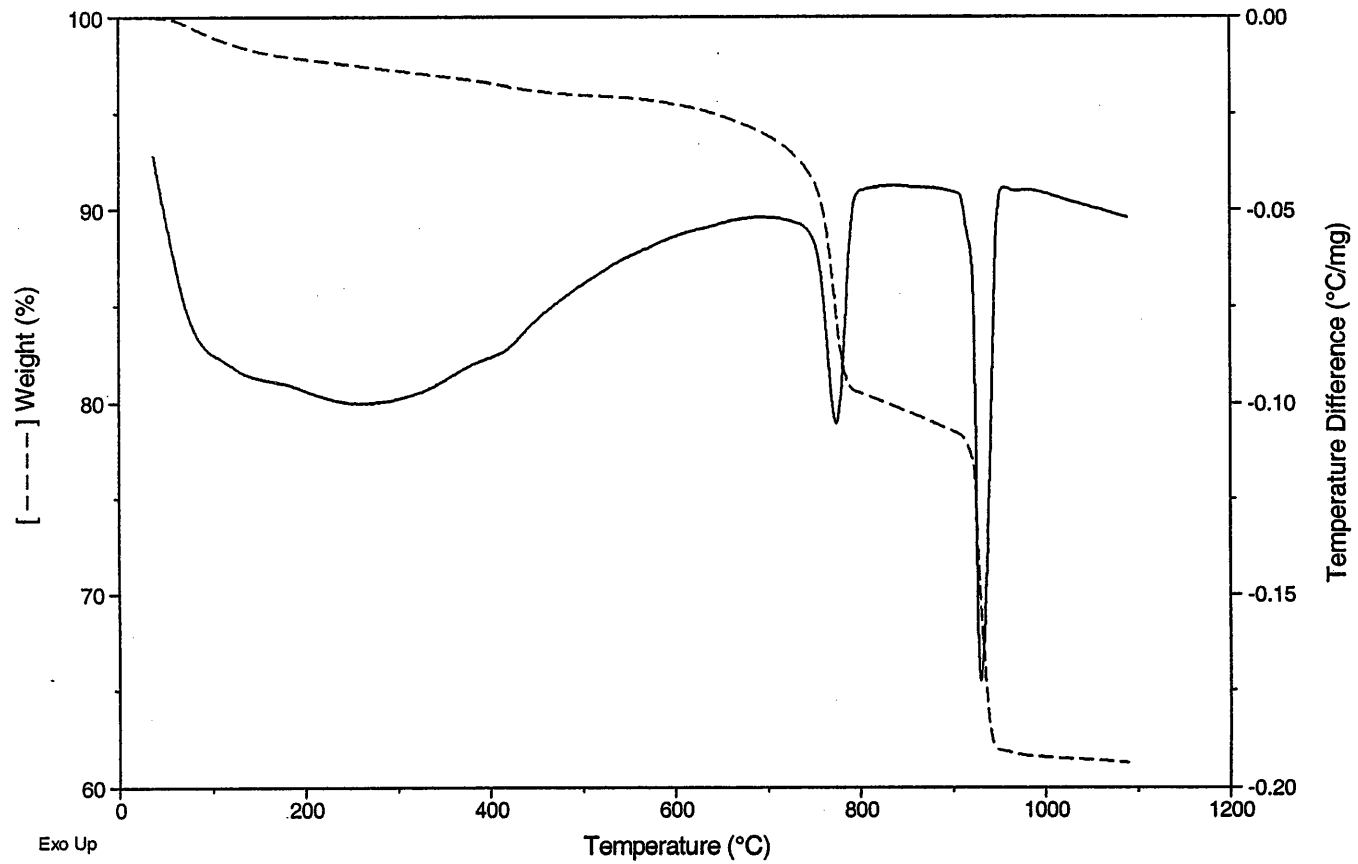


Sample: I71 # 5
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-5.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

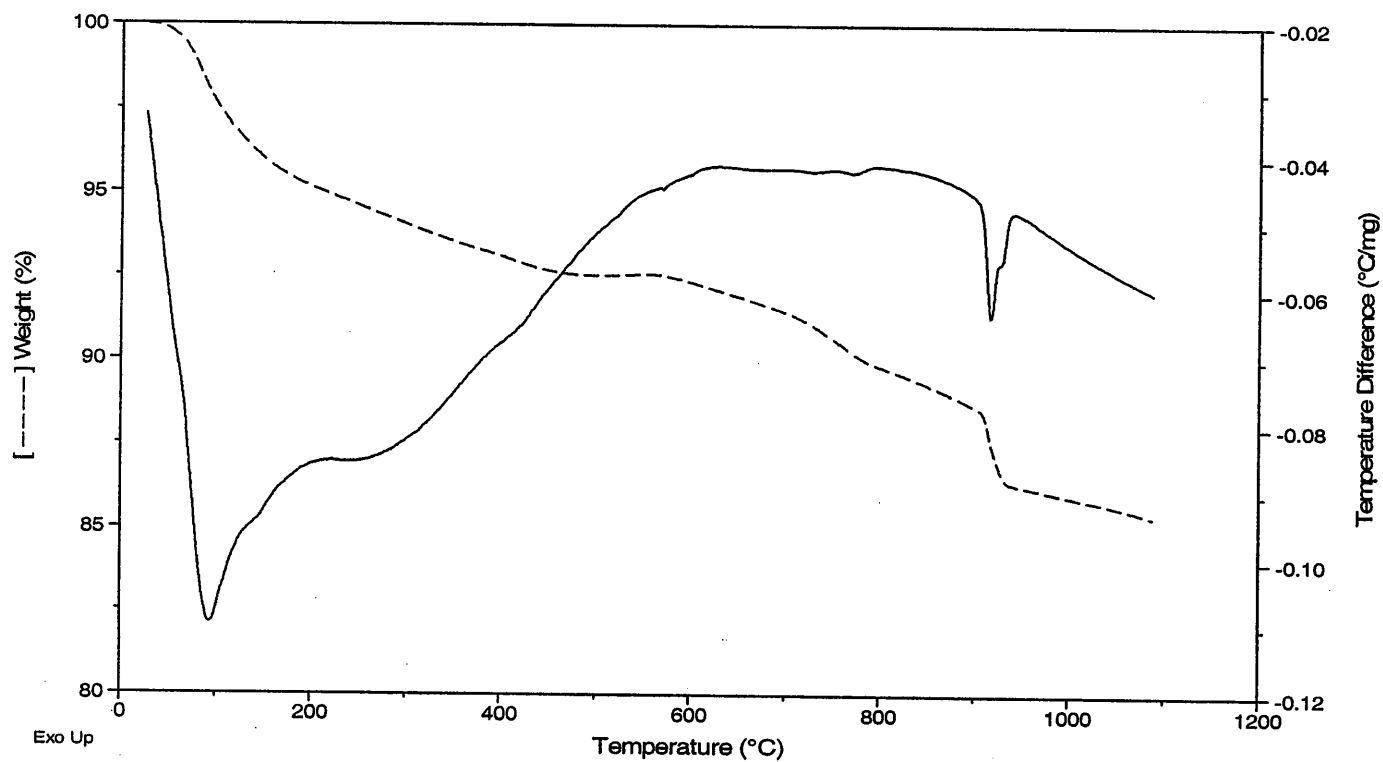


Sample: I71 # 6
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-6.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

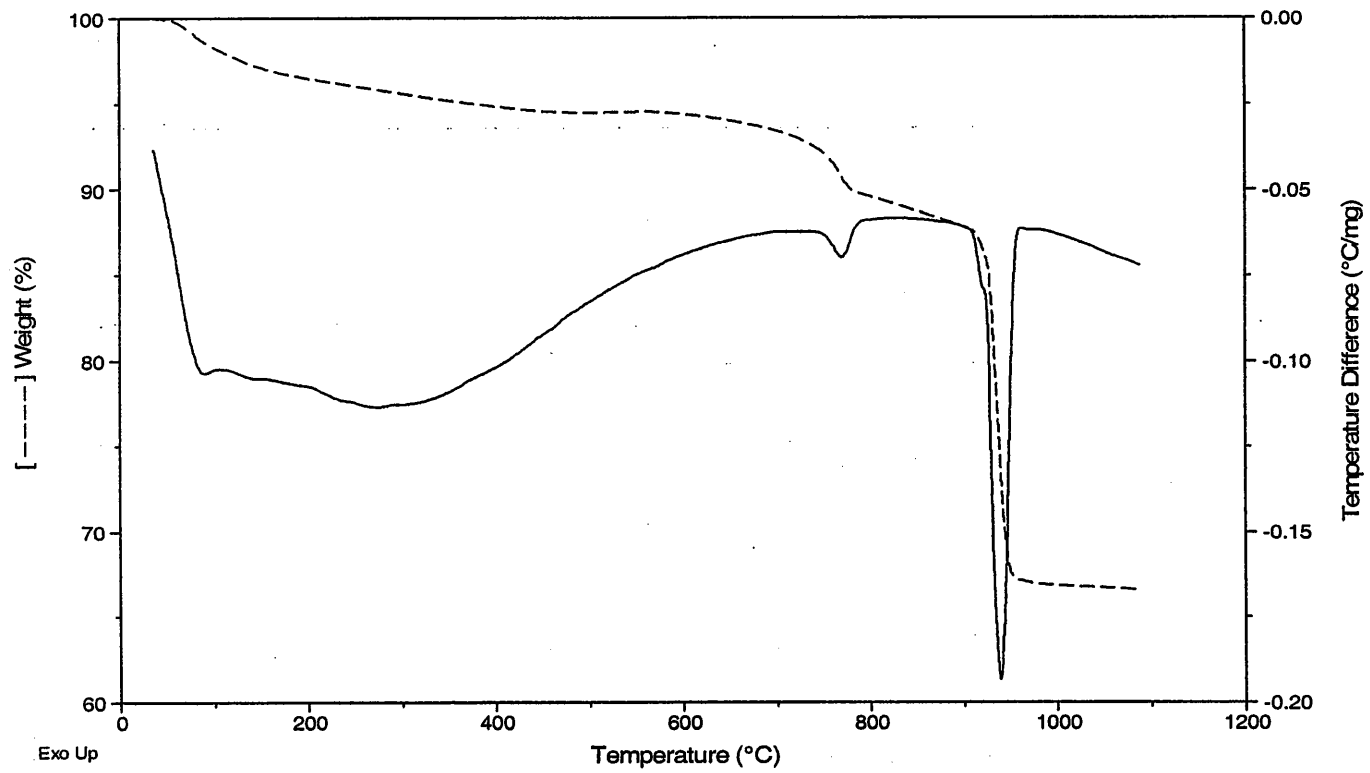


Sample: I71 # 7
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-7.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

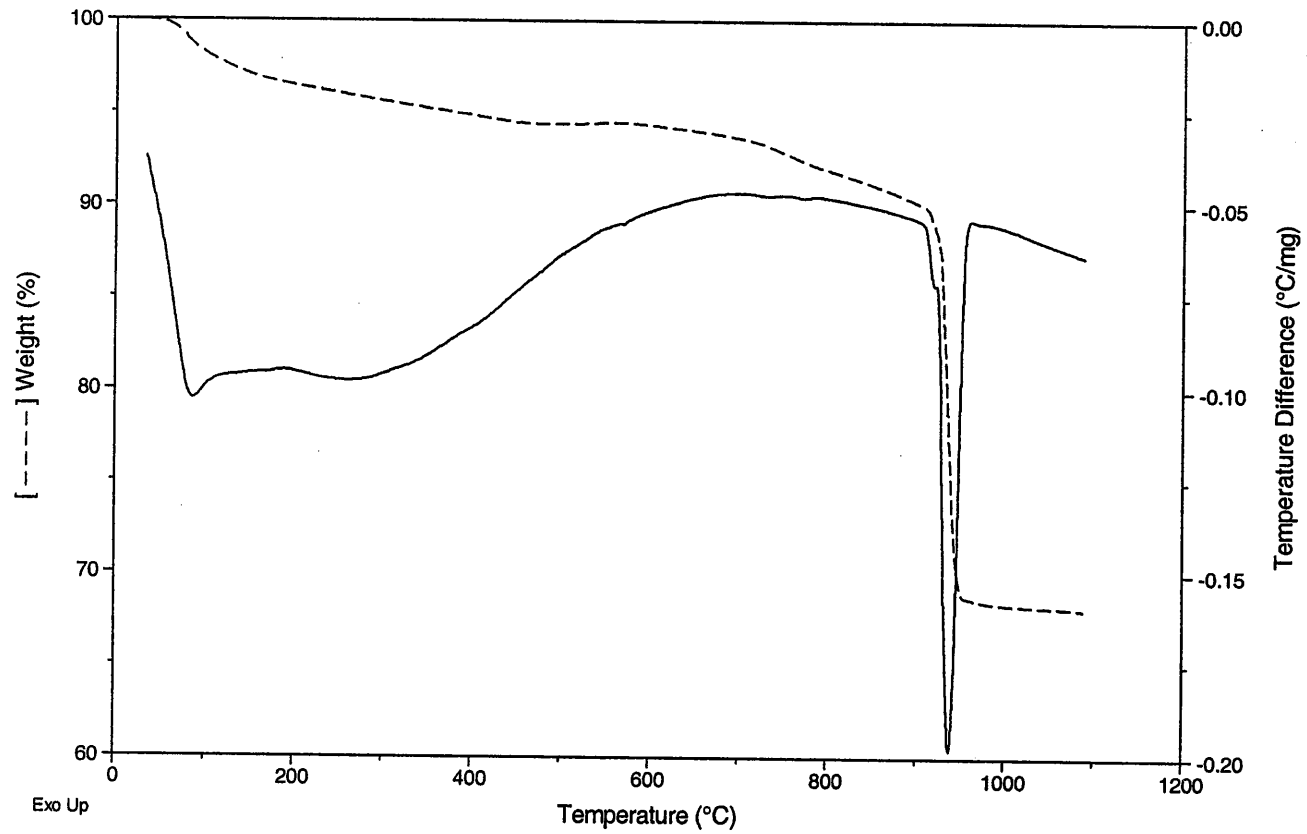


Sample: I71 # 8
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-8.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

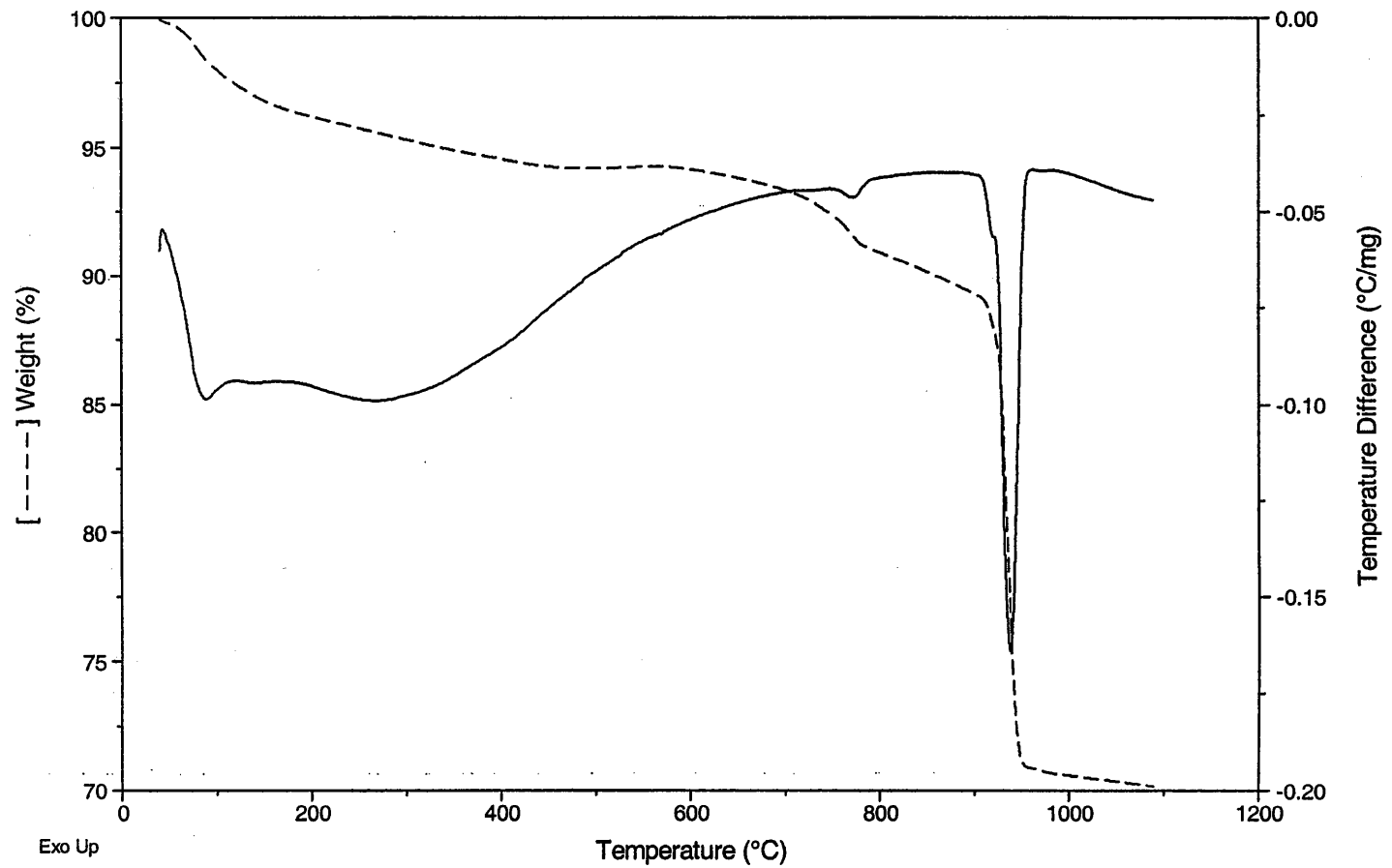


Sample: I 71 # 9
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I71-9.c02
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

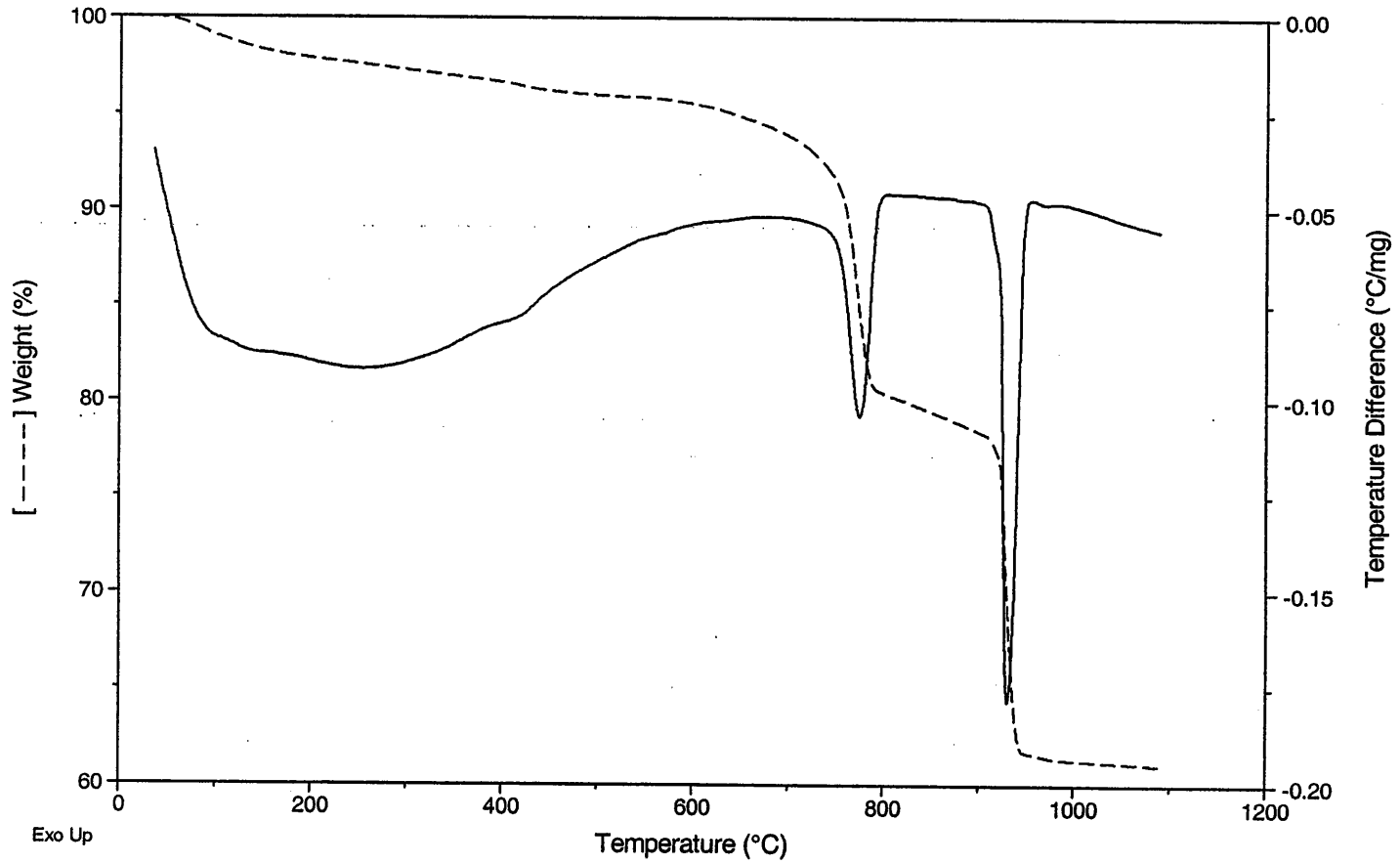


Sample: I75 # 3
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I75-3.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

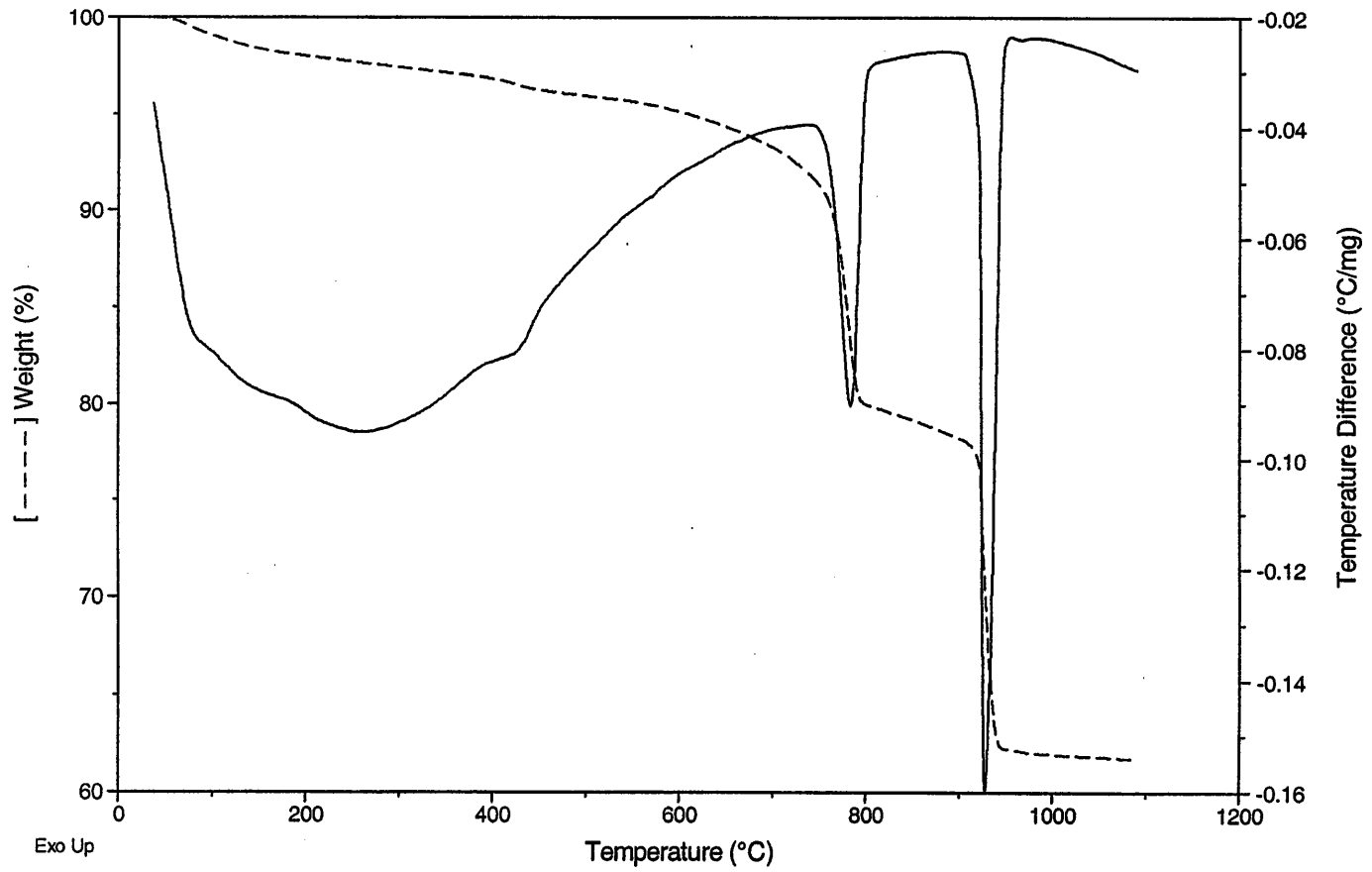


Sample: I75 # 5
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I75-5.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

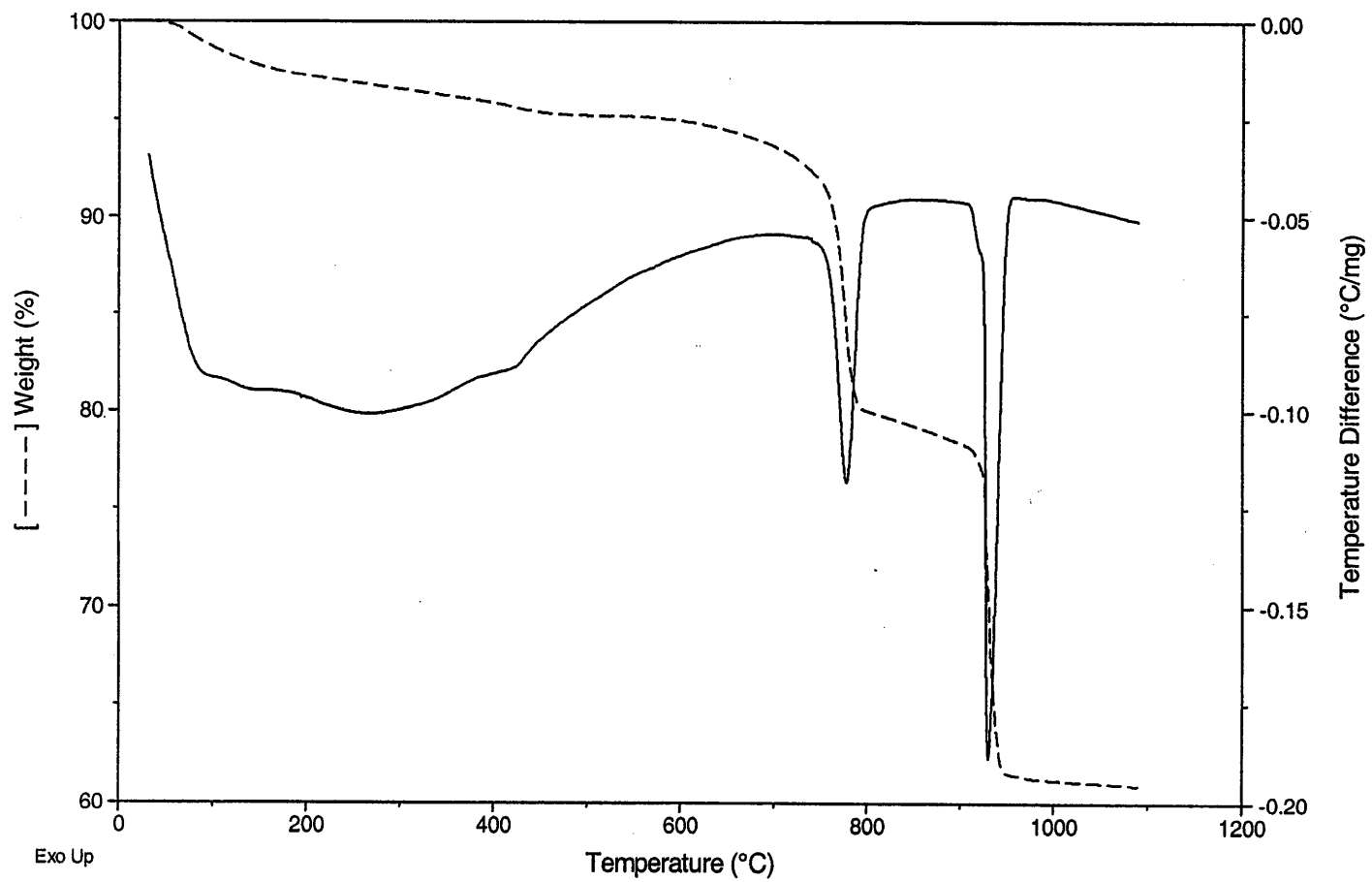


Sample: I75 # 6
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I75-6.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

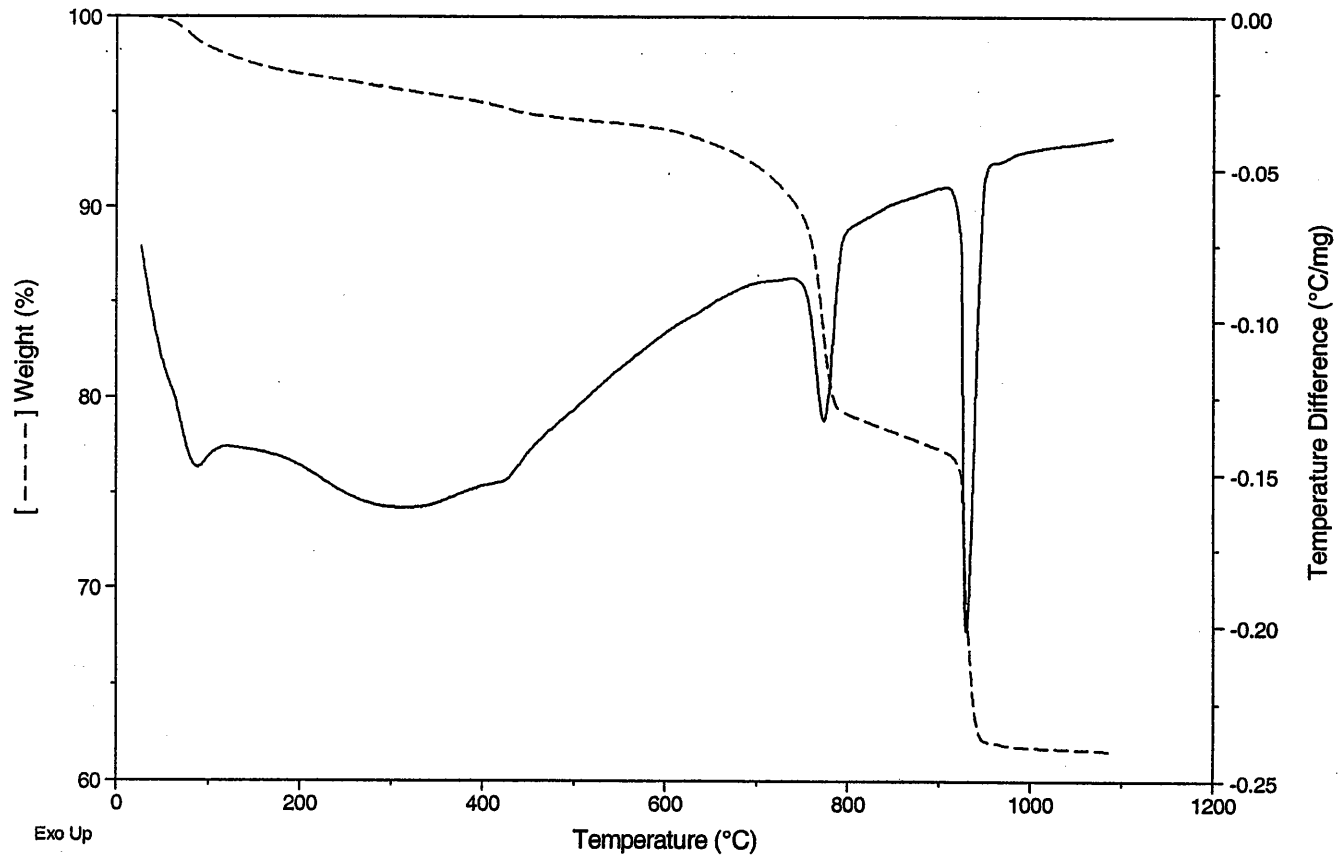


Sample: I75 # 7
Method: 10°C/min to 1100°C

TGA-DTA

File: C:\ODOT\I75-7.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

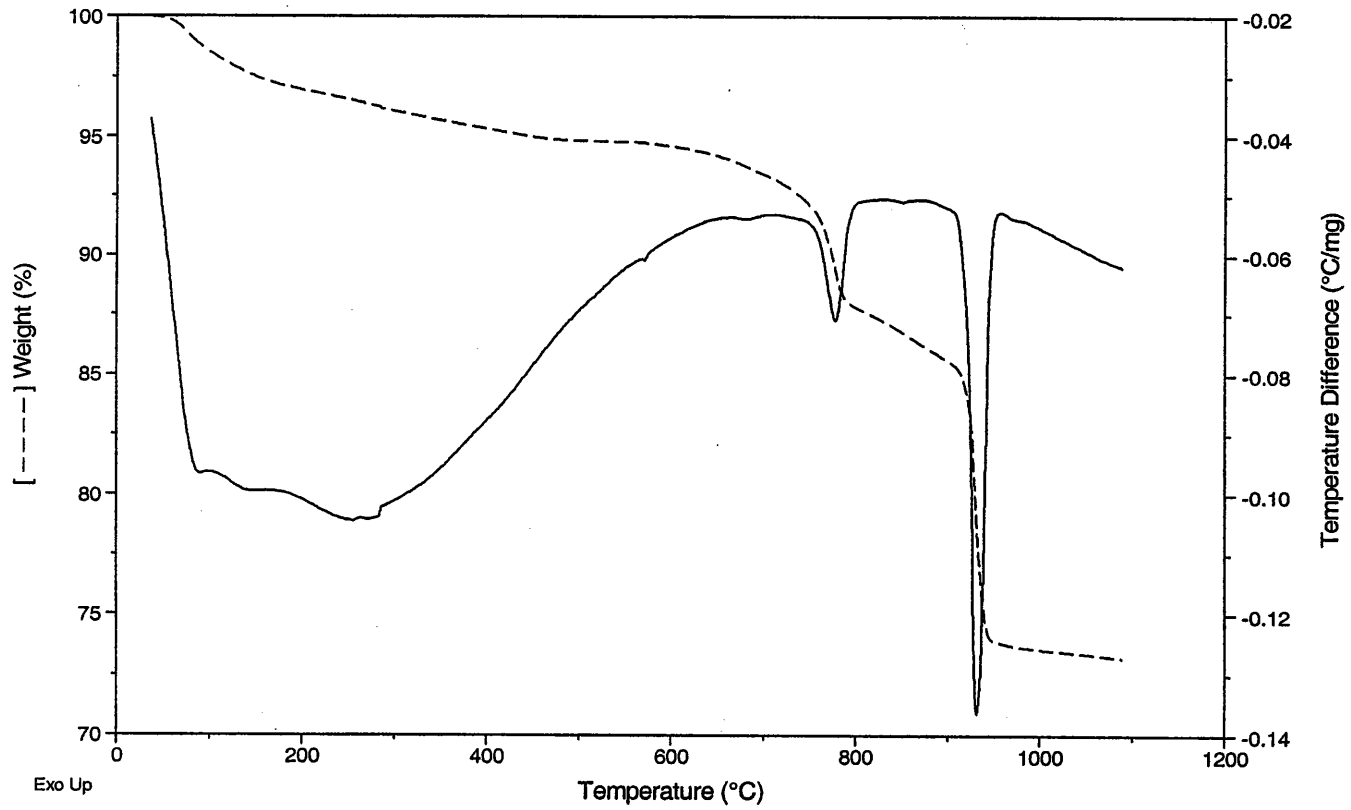


Sample: I77 # 1
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I77-1.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

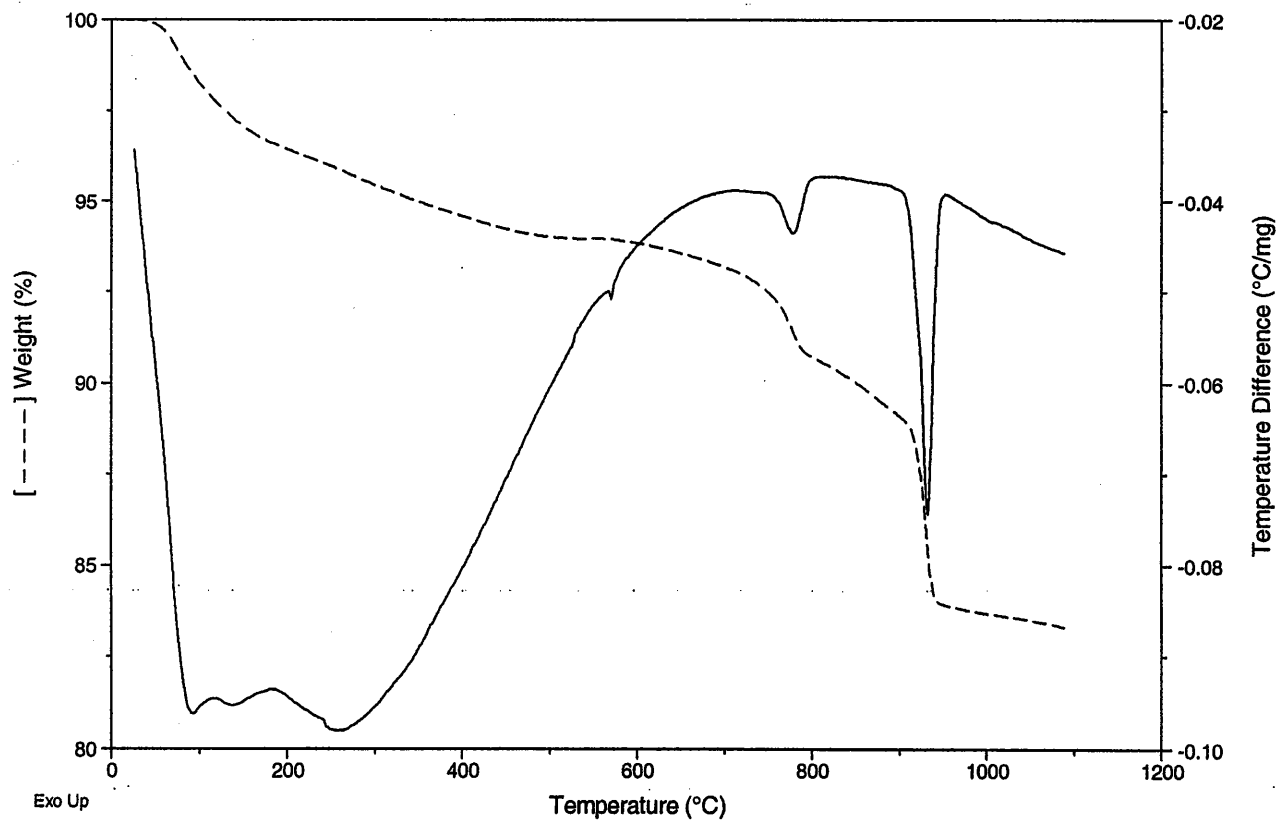


Sample: I77 # 2
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I77-2.c01
Operator: Supaporn

Comment: dry CO2, 100 mL/min

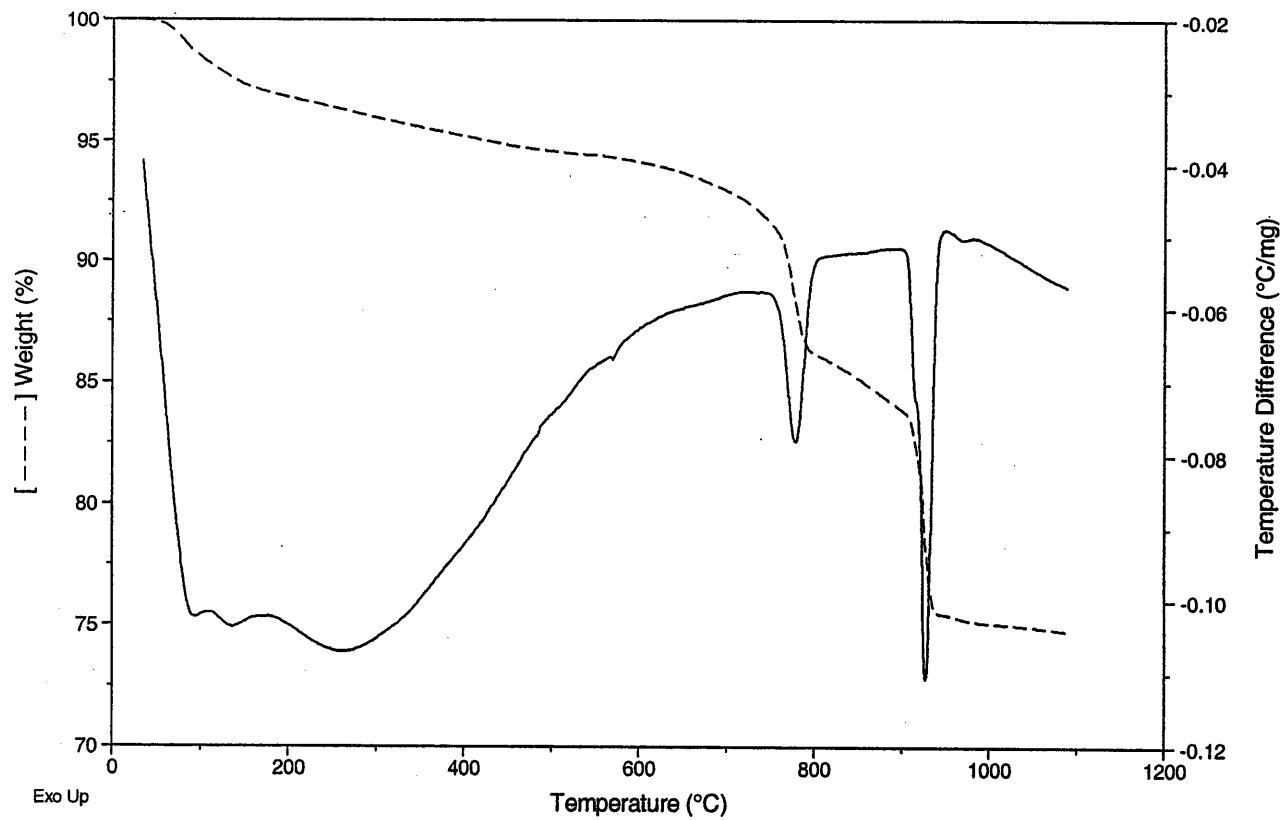


Sample: I77 #3
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I77-3.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

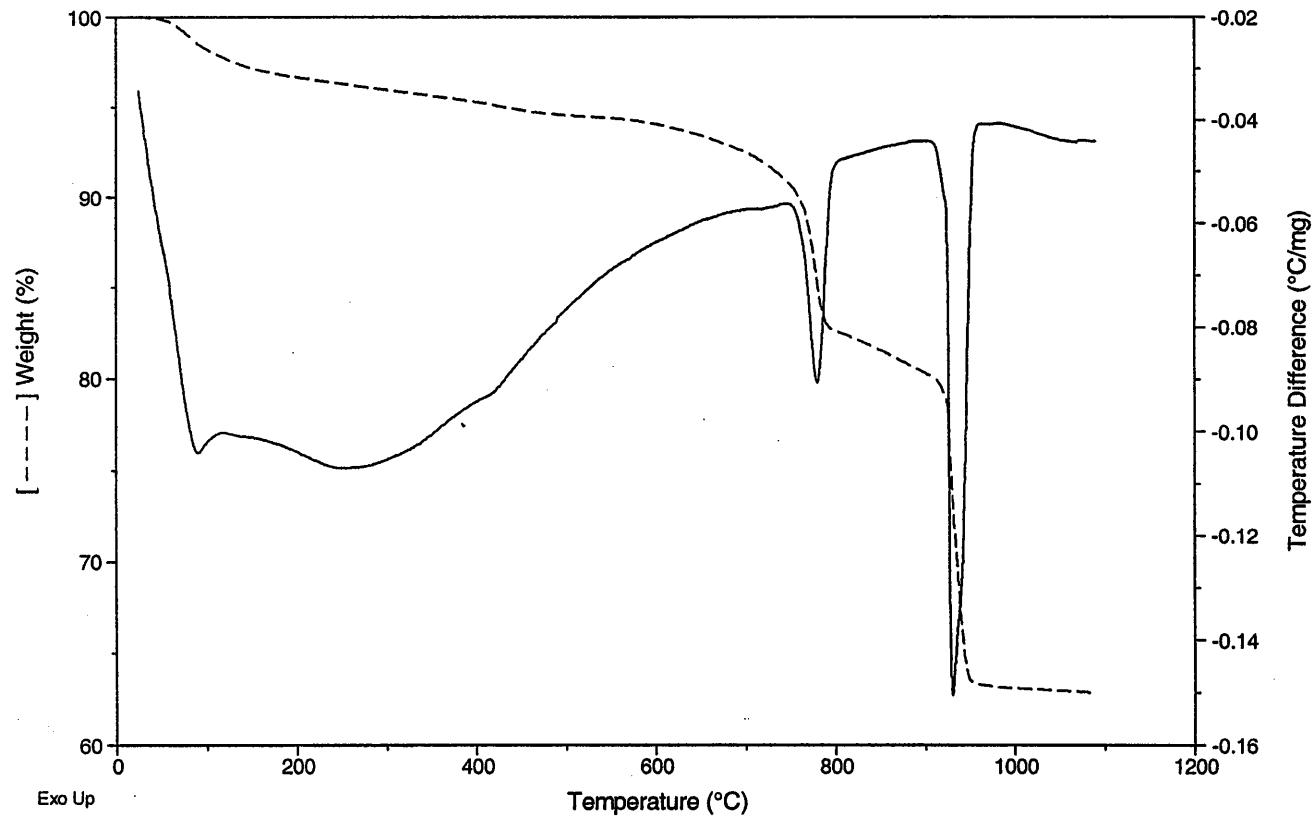


Sample: I77 # 4
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I77-4.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

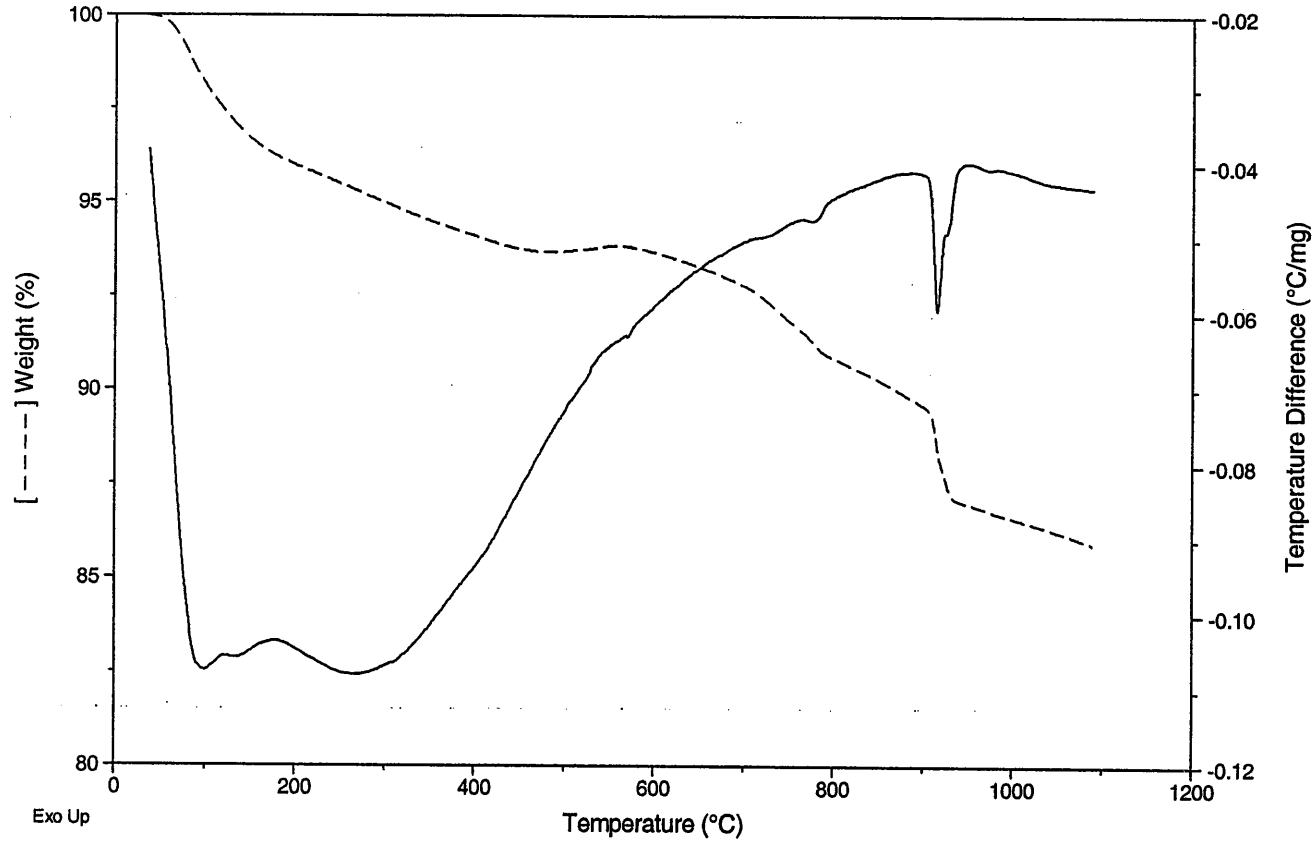


Sample: I77 # 5
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I77-5.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

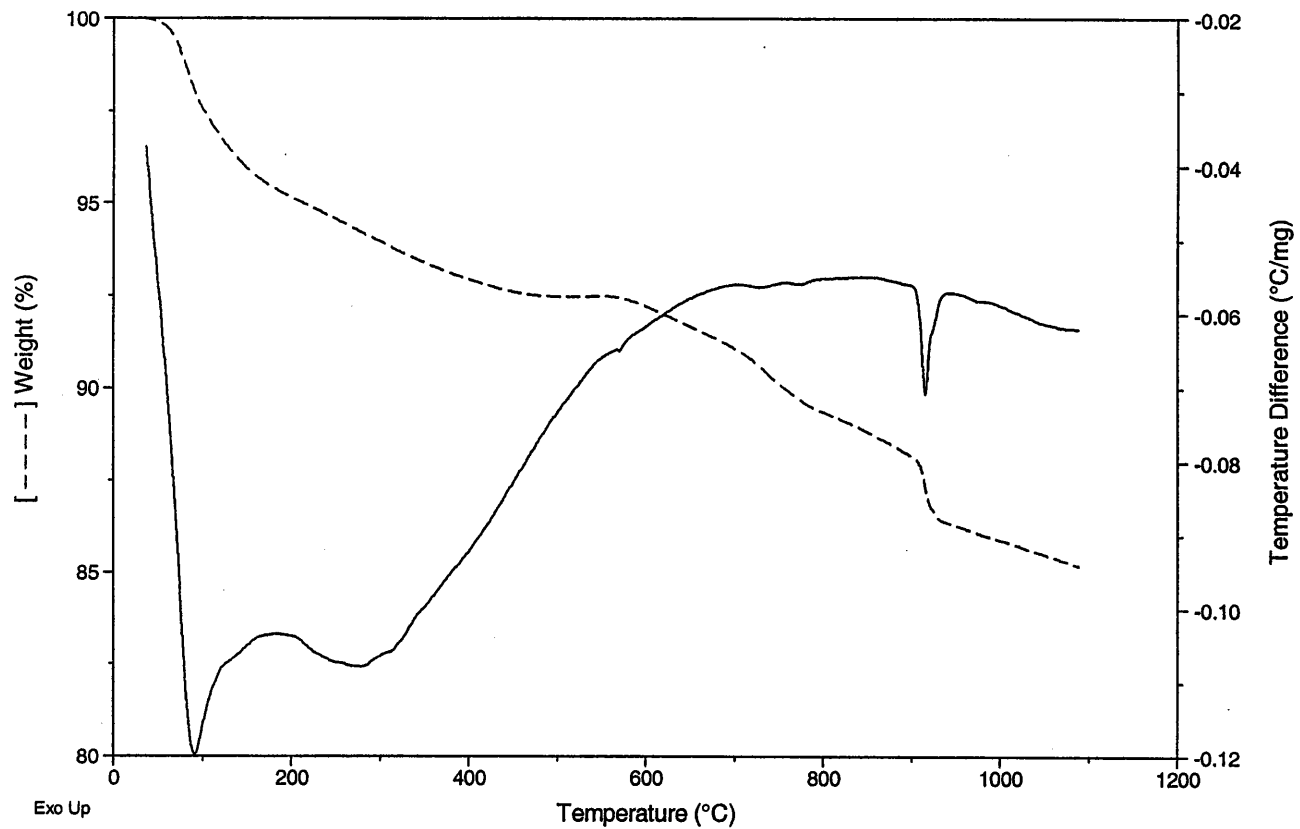


Sample: I77 # 6
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I77-6.c01
Operator: Supaporn

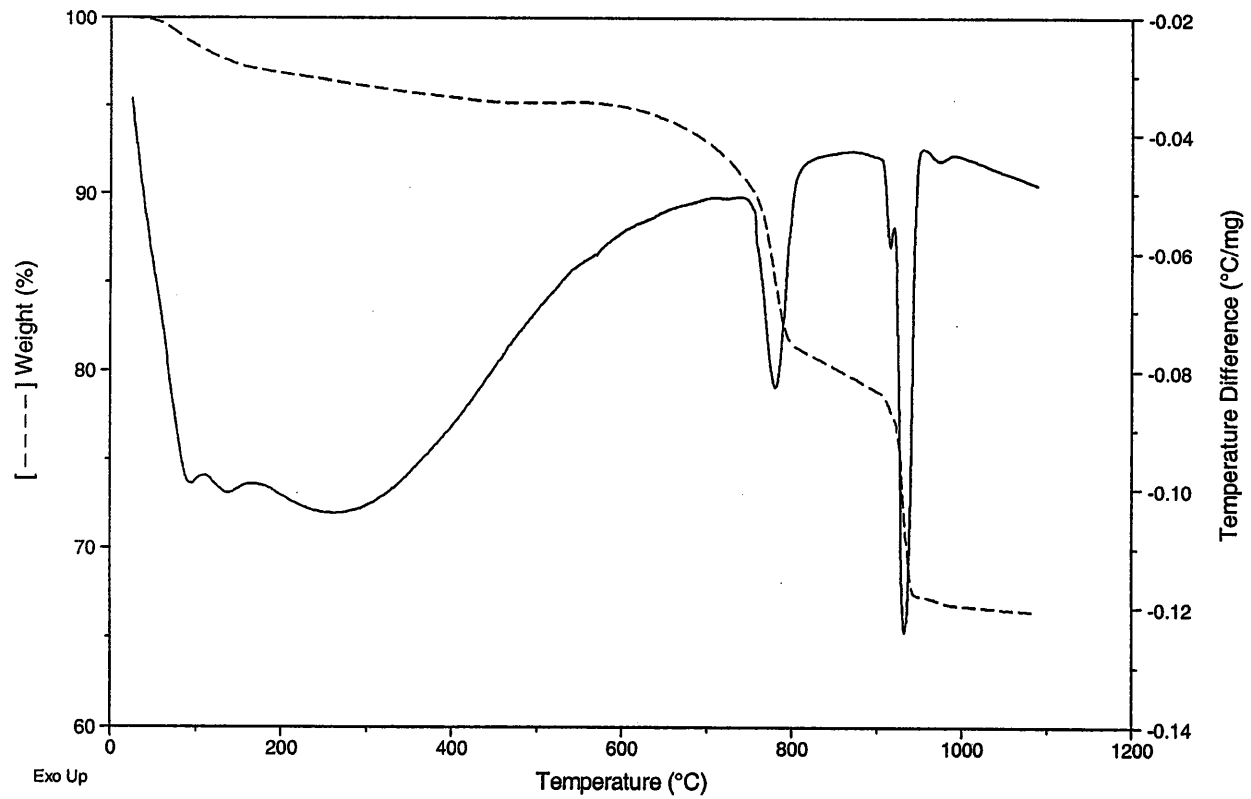
Comment: Dry CO2 100 mL/min



Sample: I77 #7
Method: 10°C/MIN TO 1100°C
Comment: Dry CO2 100 mL/min

TGA-DTA

File: C:\ODOT\I77-7.c01
Operator: Supaporn

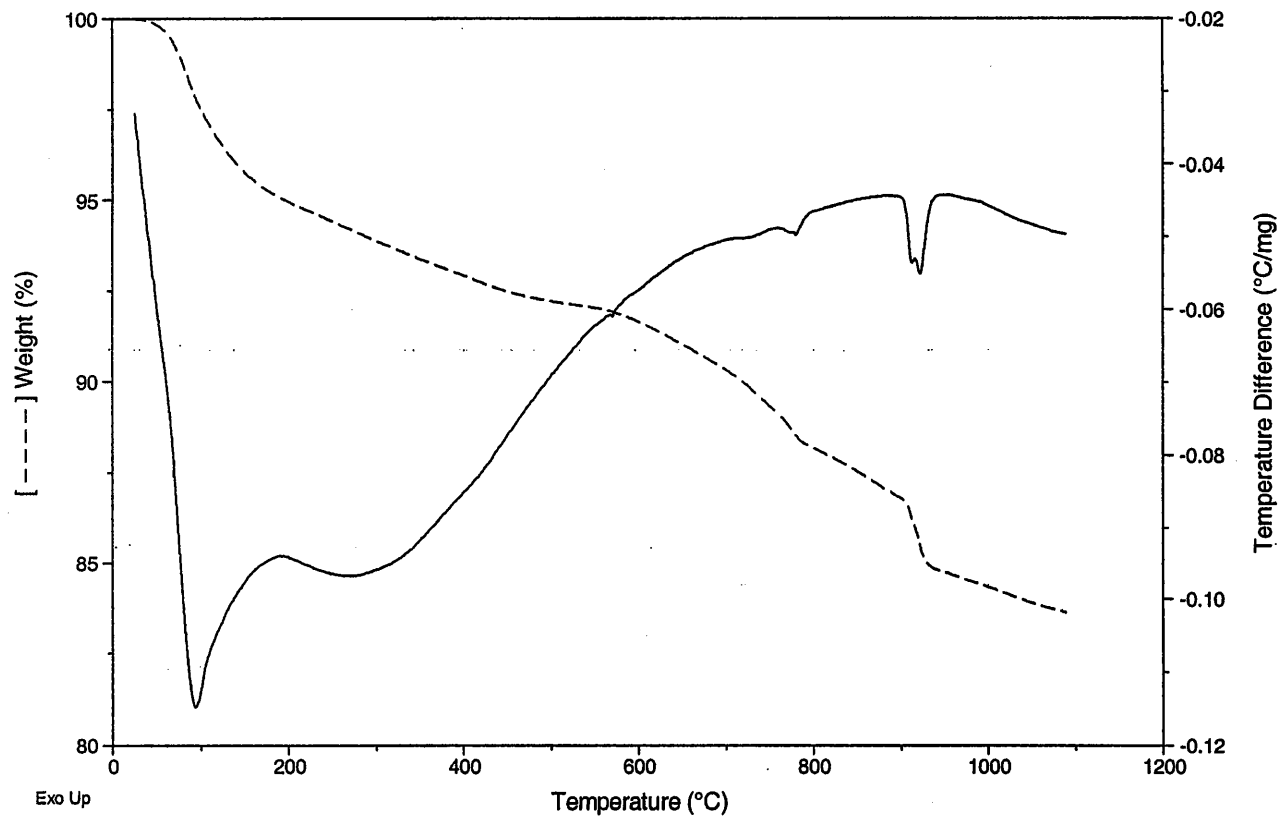


Sample: I77 # 8
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I77-8.c02
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

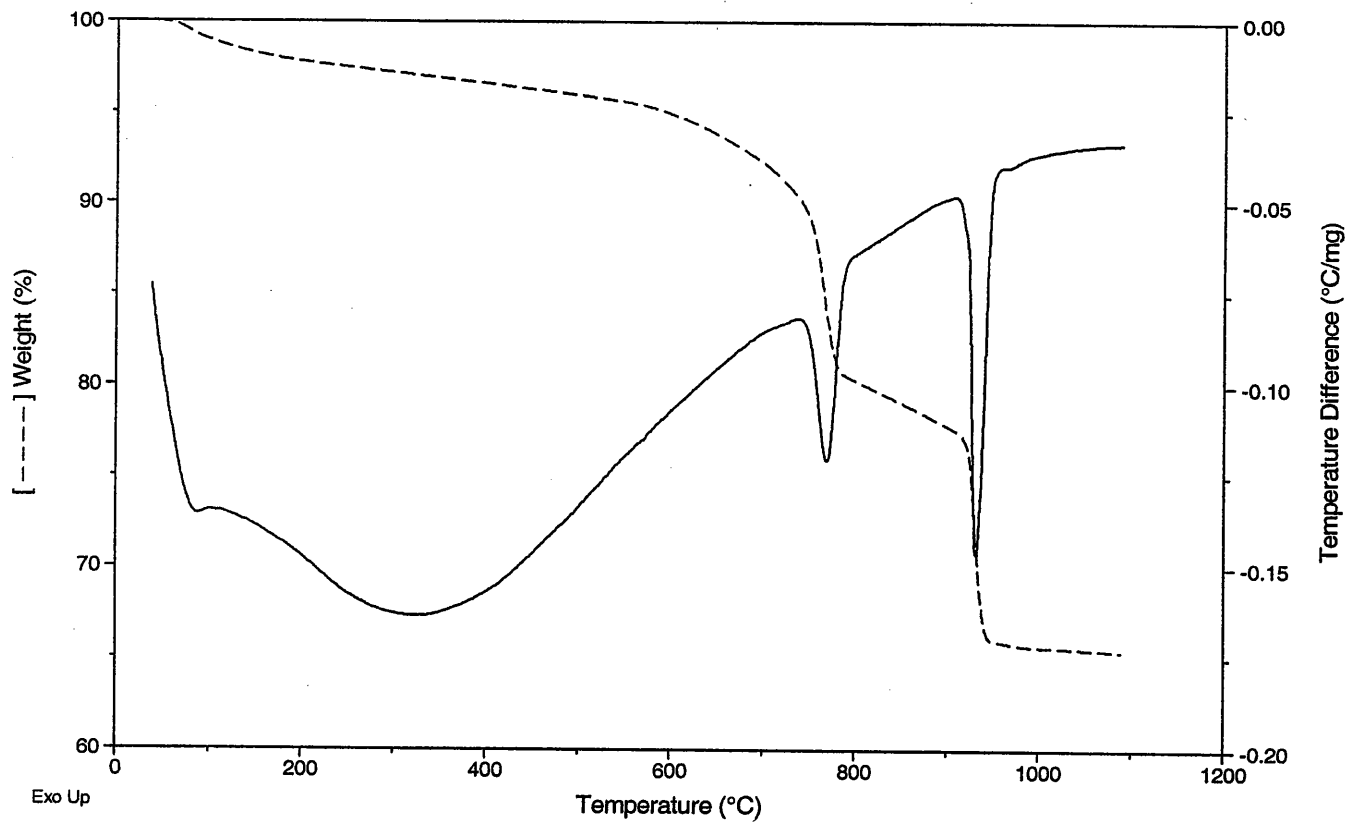


Sample: I90 # 1
Method: 10°C/min to 1100°C

TGA-DTA

File: C:\ODOT\I90-1.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

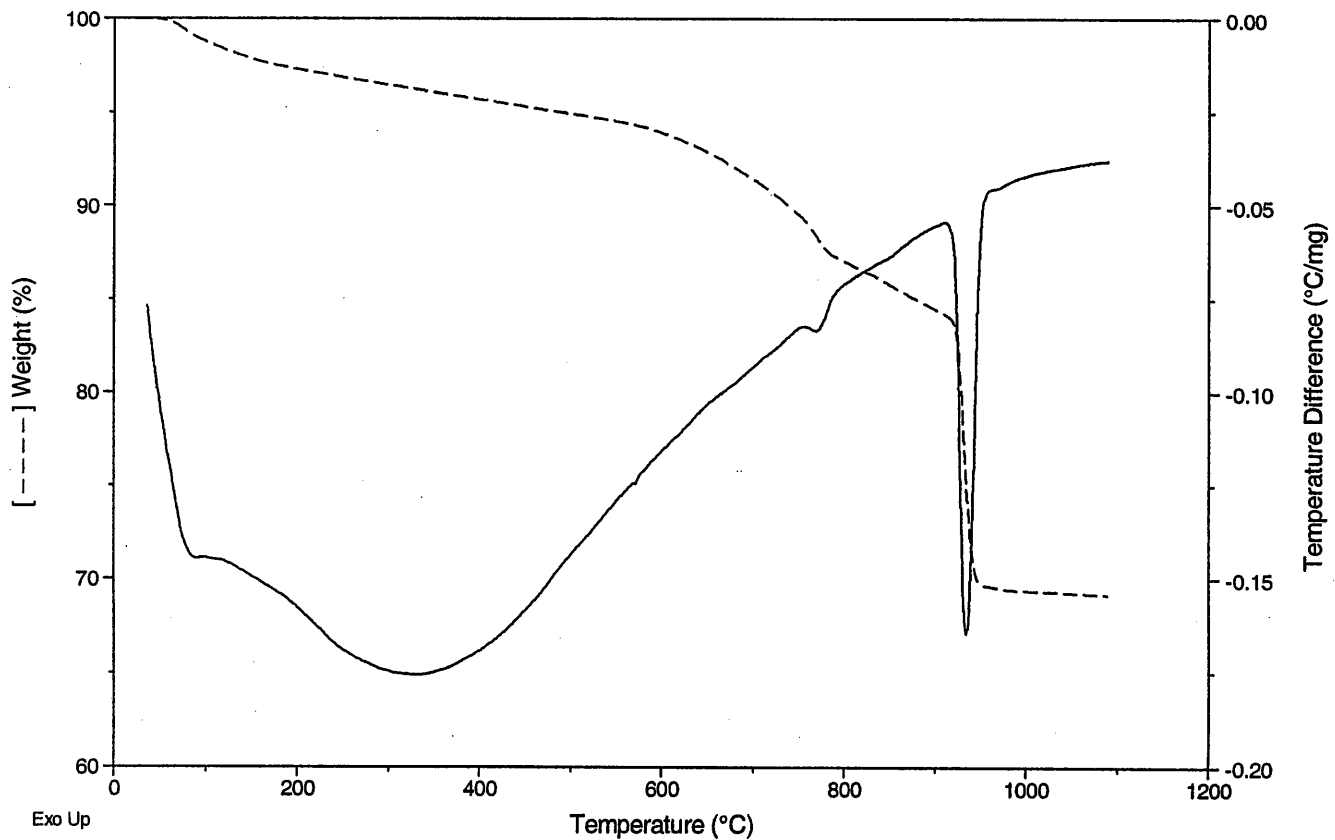


Sample: I90 # 2
Method: 10°C/min to 1100°C

TGA-DTA

File: C:\ODOT\I90-2.c01
Operator: Supaporn

Comment: Dry CO2 100 mL/min

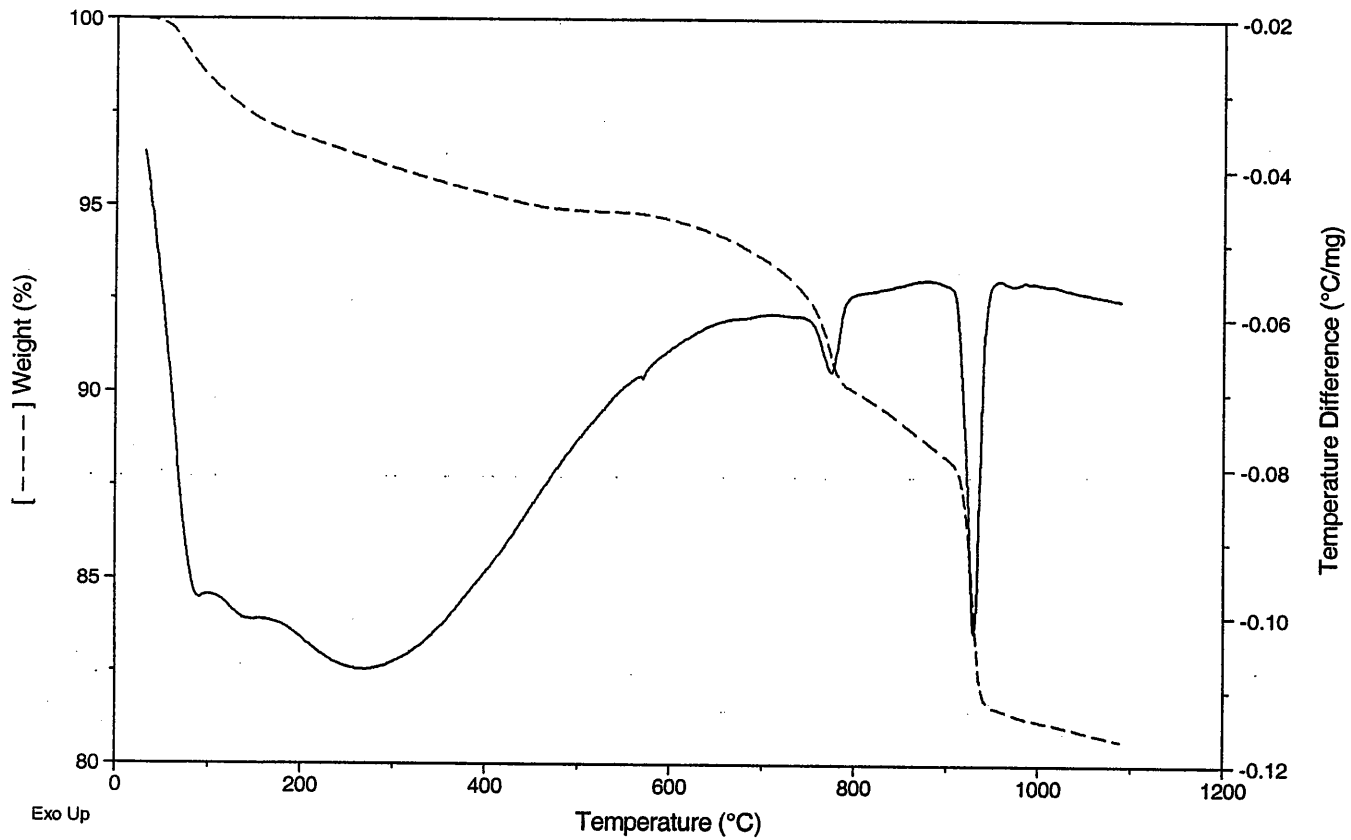


Sample: I90 # 3
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I90-3.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

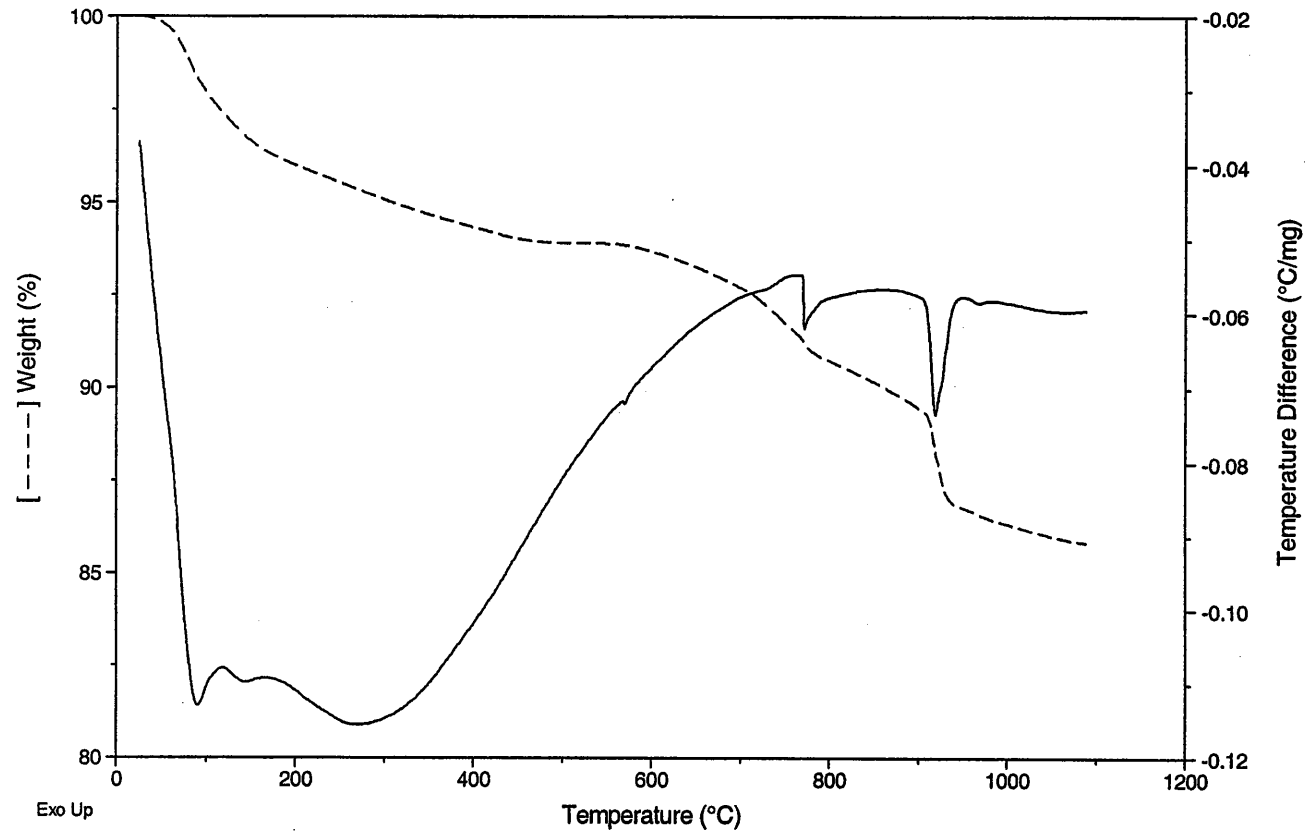


Sample: I90 # 4
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I90-4.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

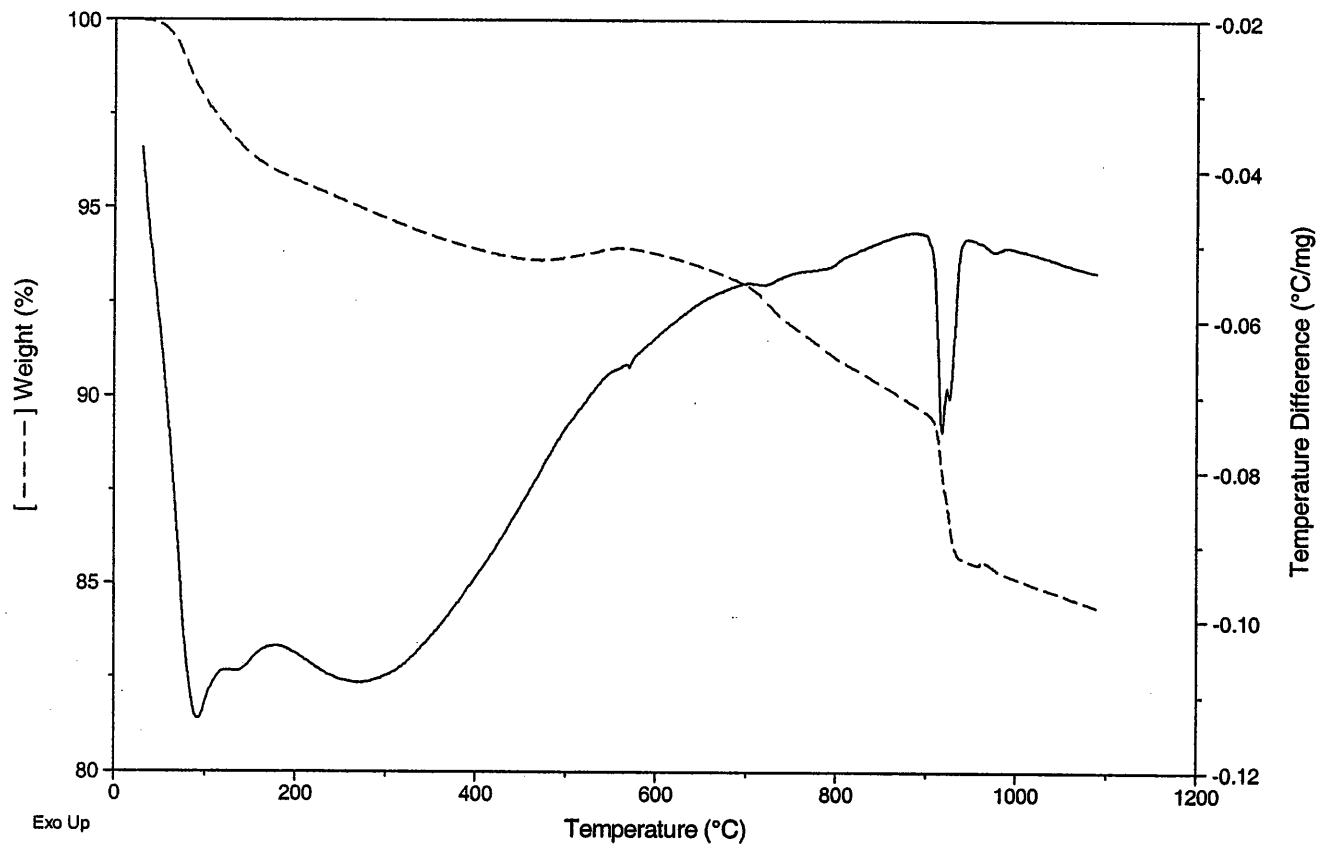


Sample: I90 # 5
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I90-5.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min

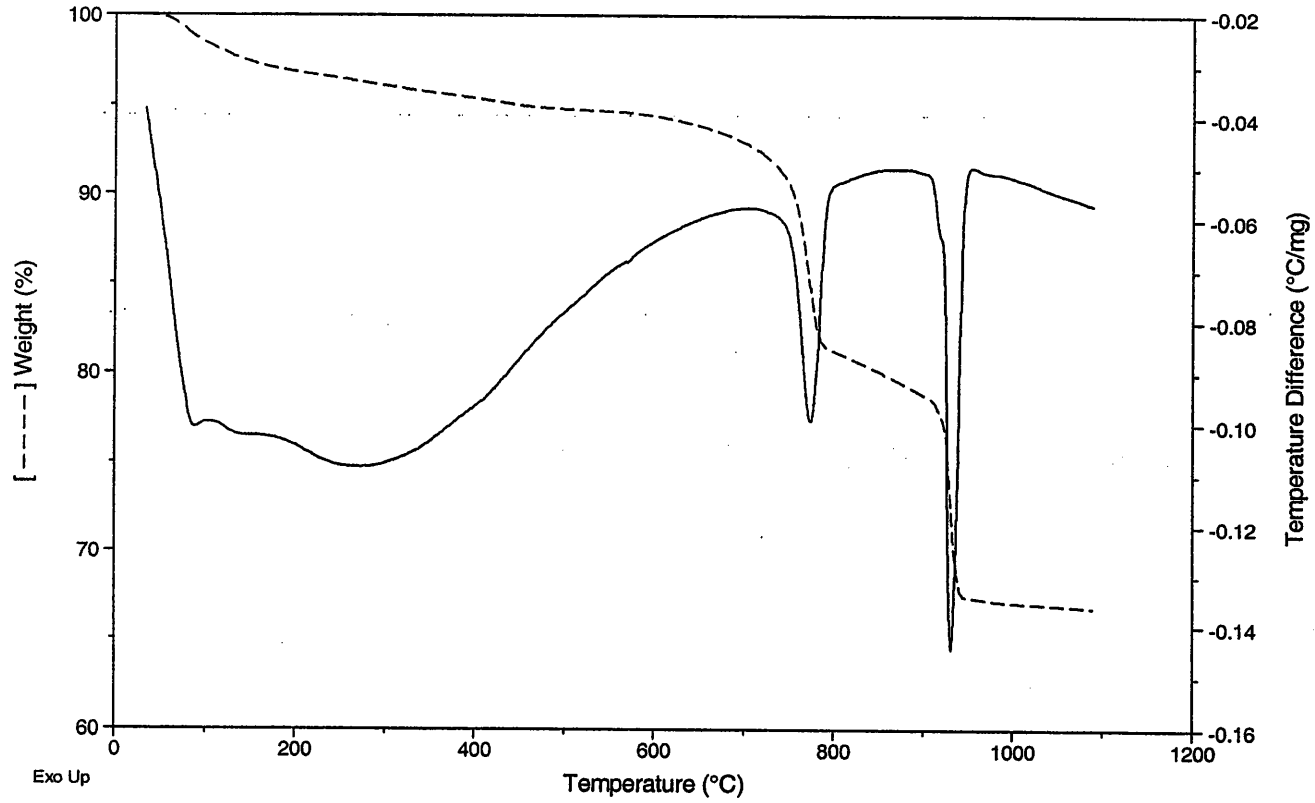


Sample: I90 # 6
Method: 10°C/MIN TO 1100°C

TGA-DTA

File: C:\ODOT\I90-6.c01
Operator: Supaporn

Comment: Dry CO2, 100 mL/min



Appendix B, Section 2

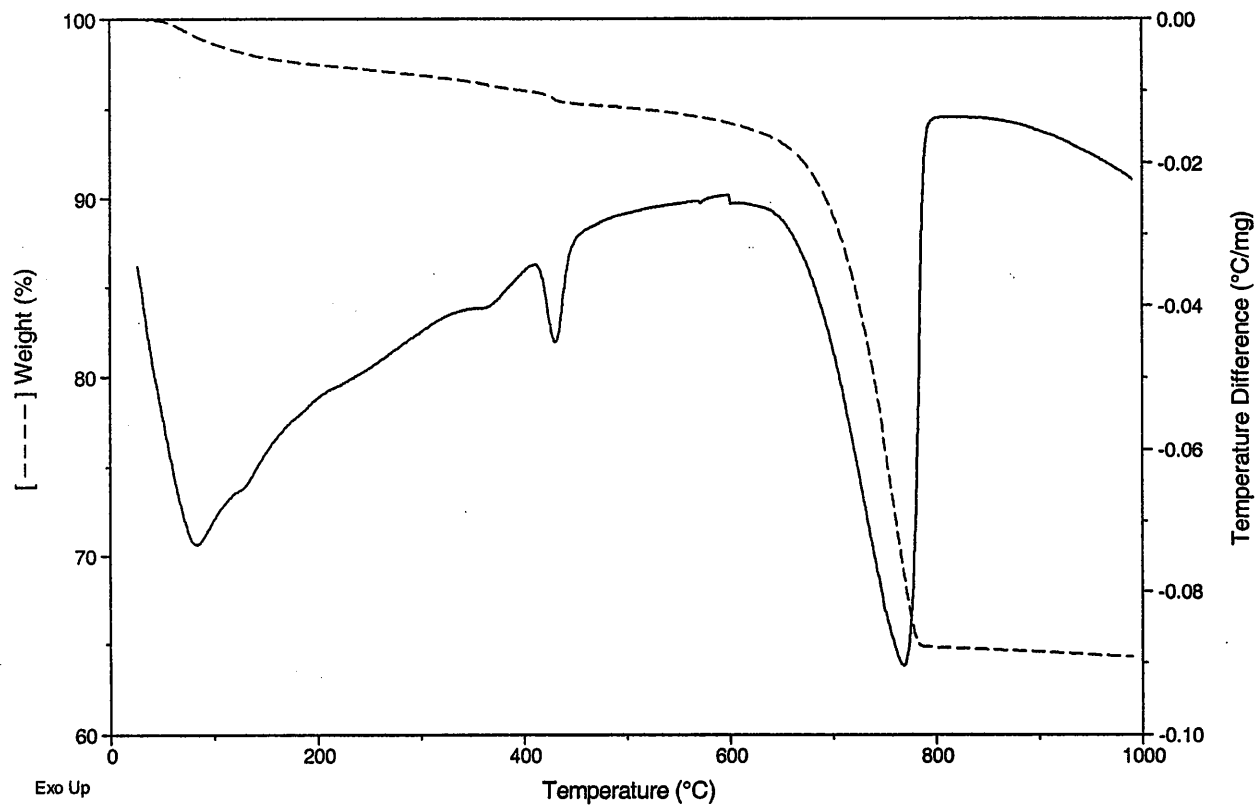
The TG-DTA Plots for all the RPCC Aggregates tested in N₂ Atmosphere

Sample: I-70 # 1
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-1.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

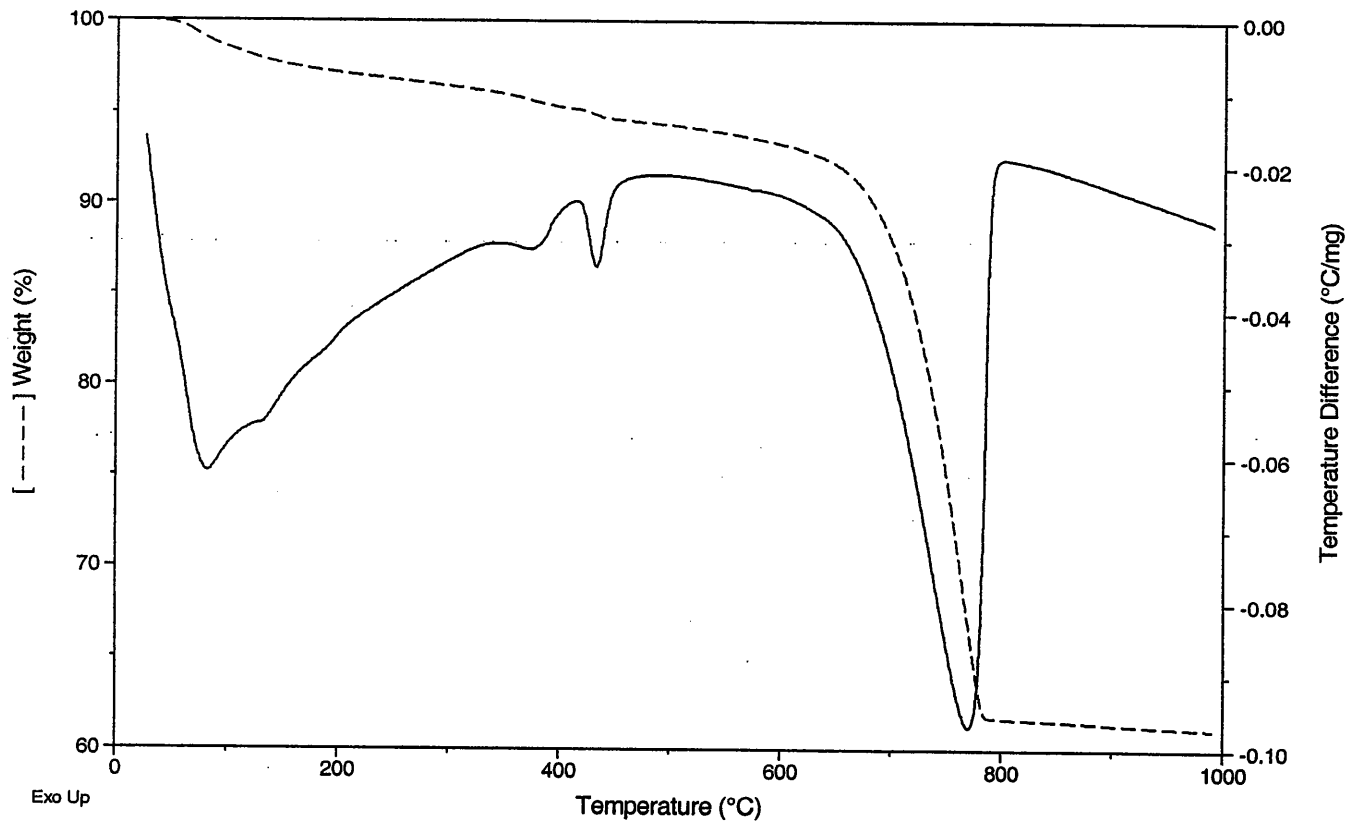


Sample: I70 # 2
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-2.n02
Operator: Supaporn

Comment: Dry N2, 100 mL/min

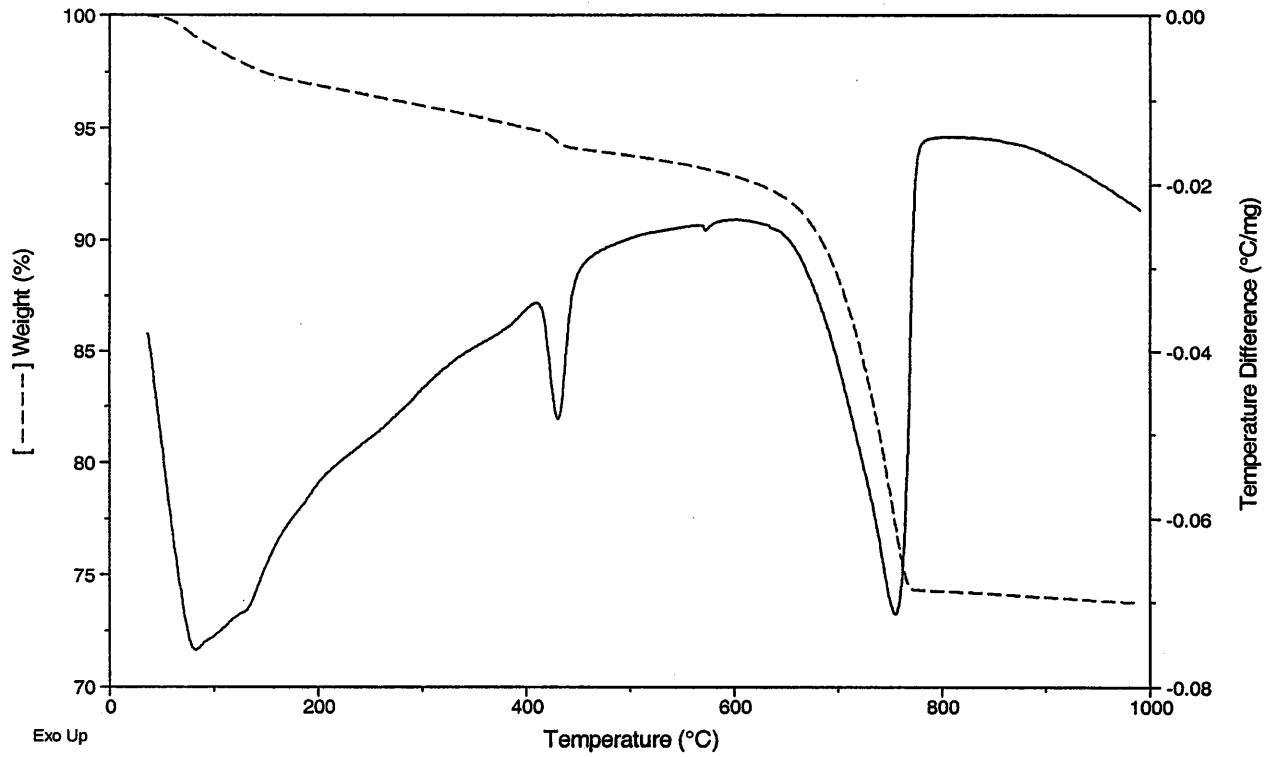


Sample: I-70 # 3
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-3.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

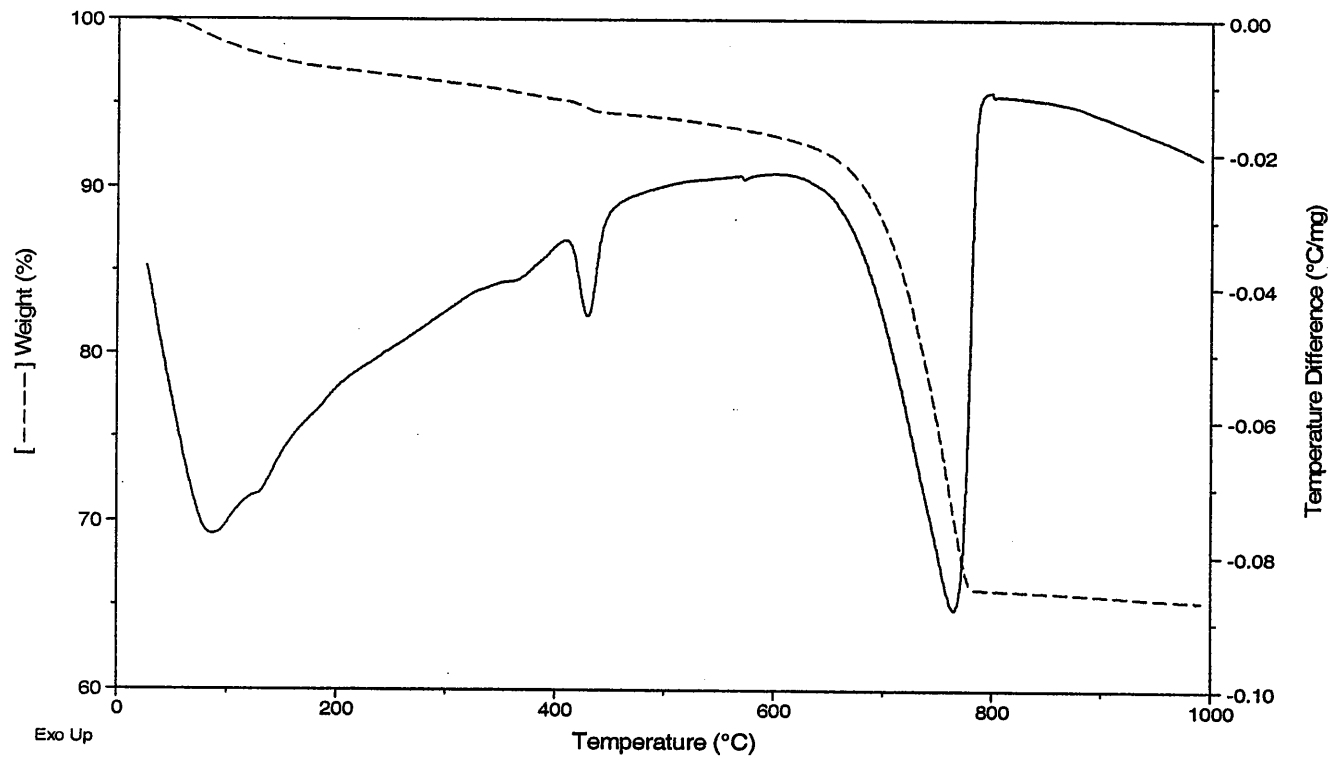


Sample: I-70 # 4
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-4.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

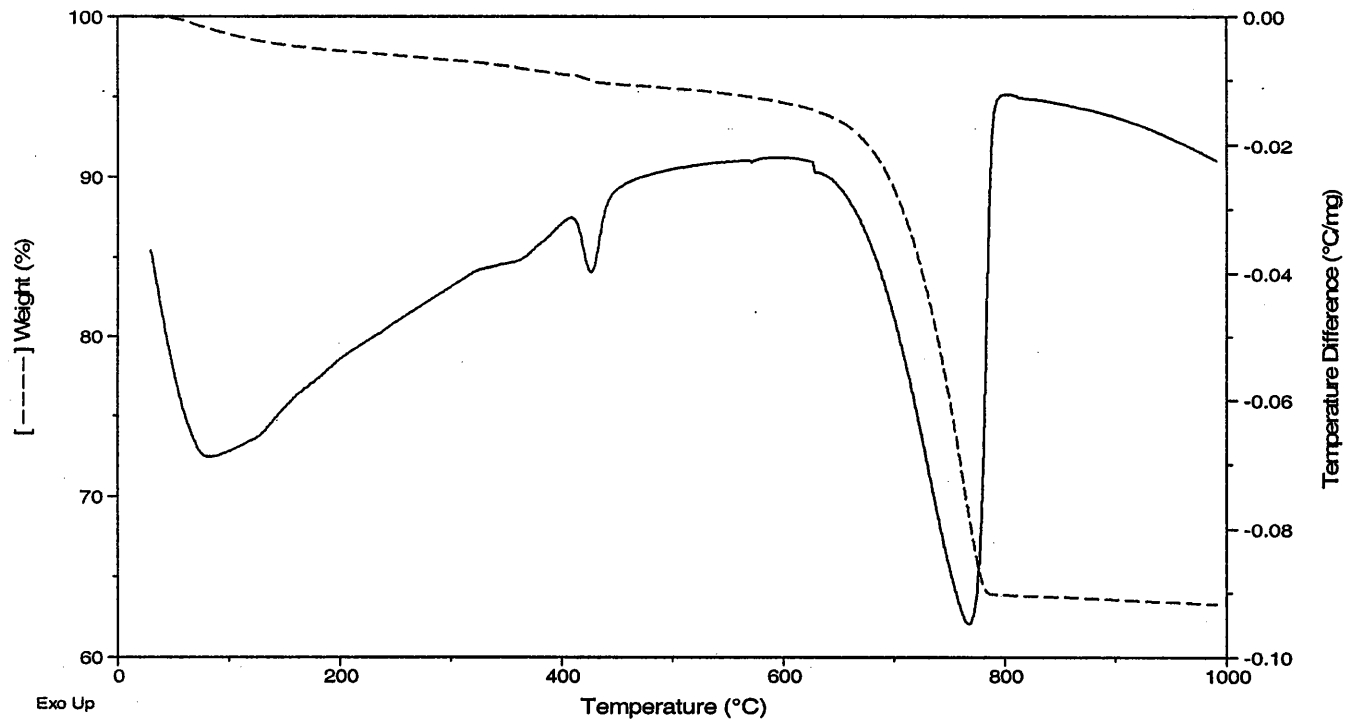


Sample: I70 # 5
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-5.n01
Operator: Supaporn

Comment: Dry N2 100 mL/min

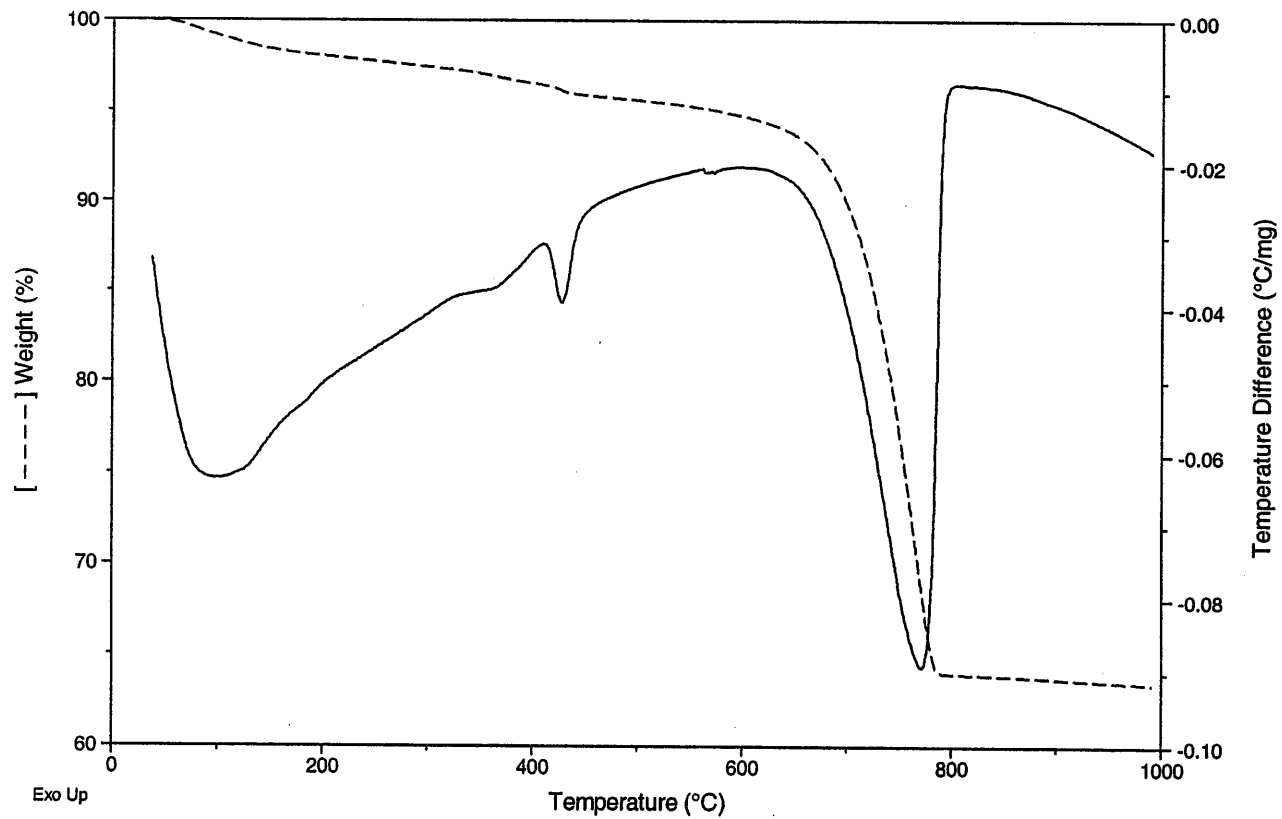


Sample: I70 # 6
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-6.n01
Operator: Supaporn

Comment: Dry N2 100 mL/min

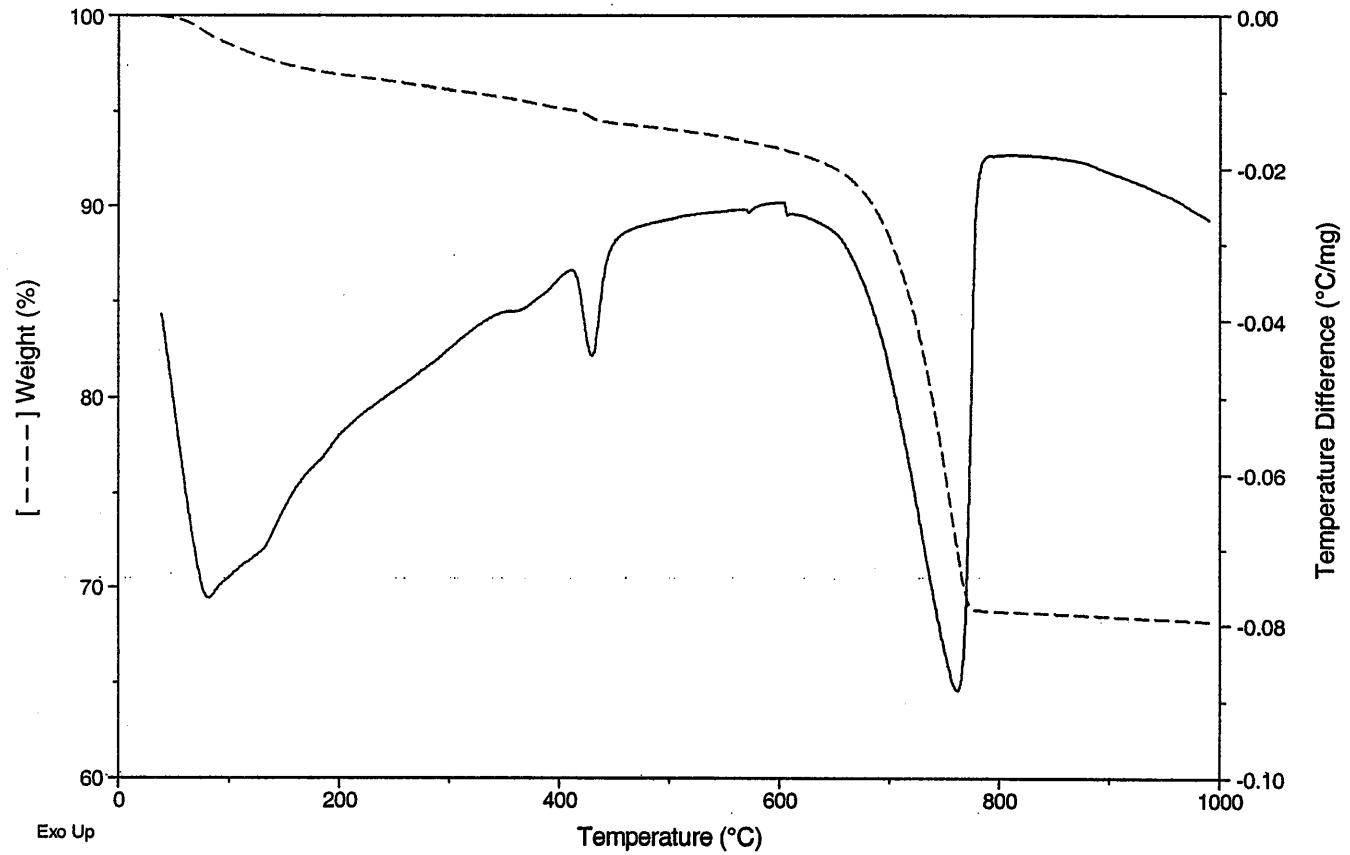


Sample: I70 # 7
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-7.n01
Operator: Supaporn

Comment: Dry N2 100 mL/min

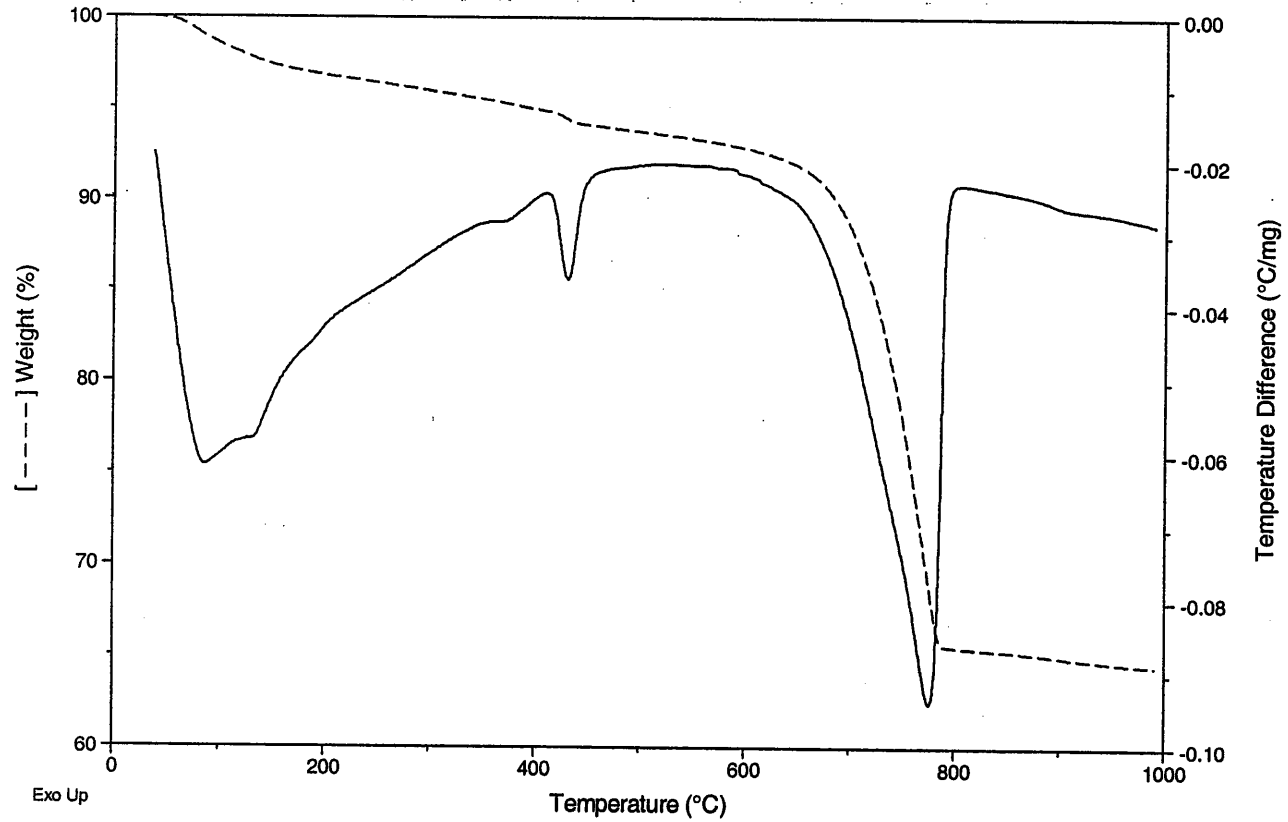


Sample: I70 # 8
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-8.n02
Operator: Supaporn

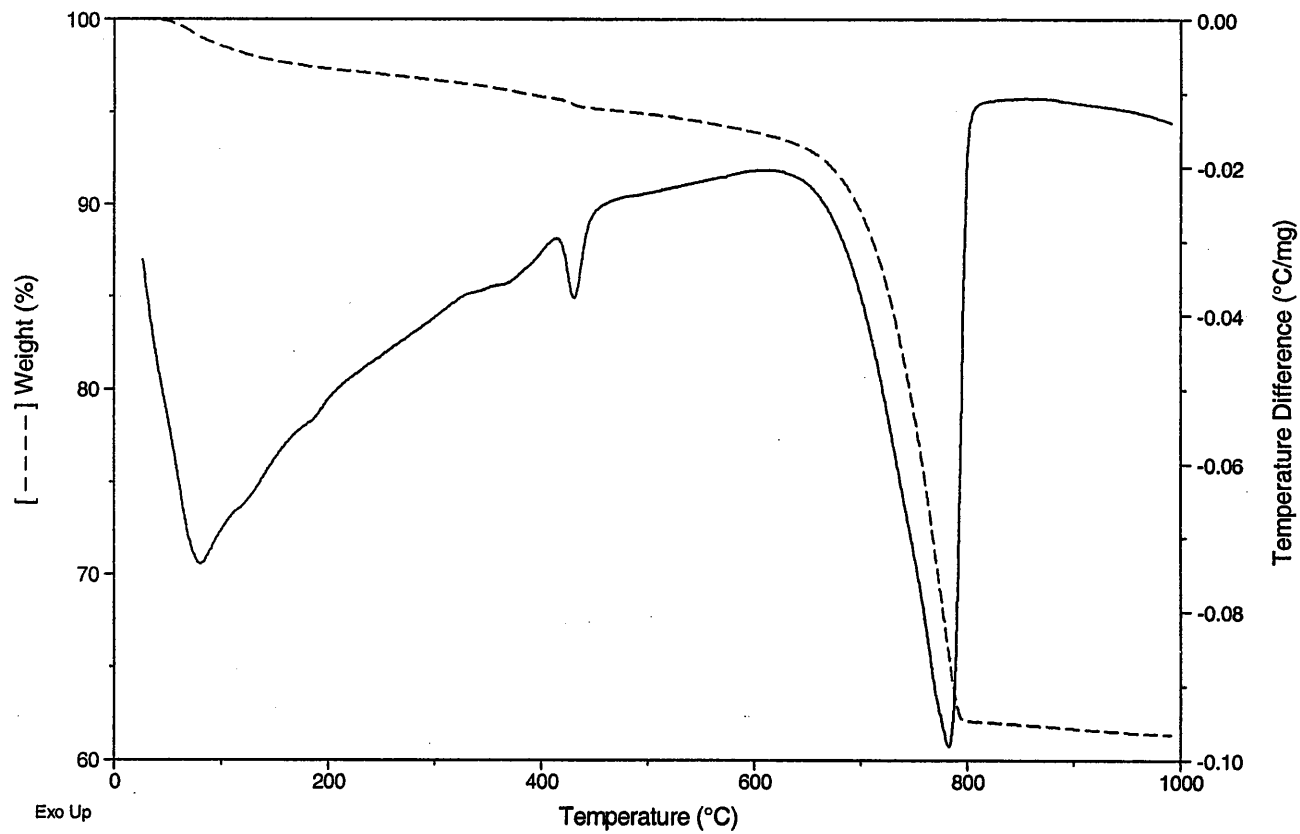
Comment: Dry N2, 100 mL/min



Sample: I70 # 9
Method: 10°C/MIN TO 1000°C
Comment: Dry N2 100 mL/min

TGA-DTA

File: C:\ODOT\I70-9.n01
Operator: Supaporn

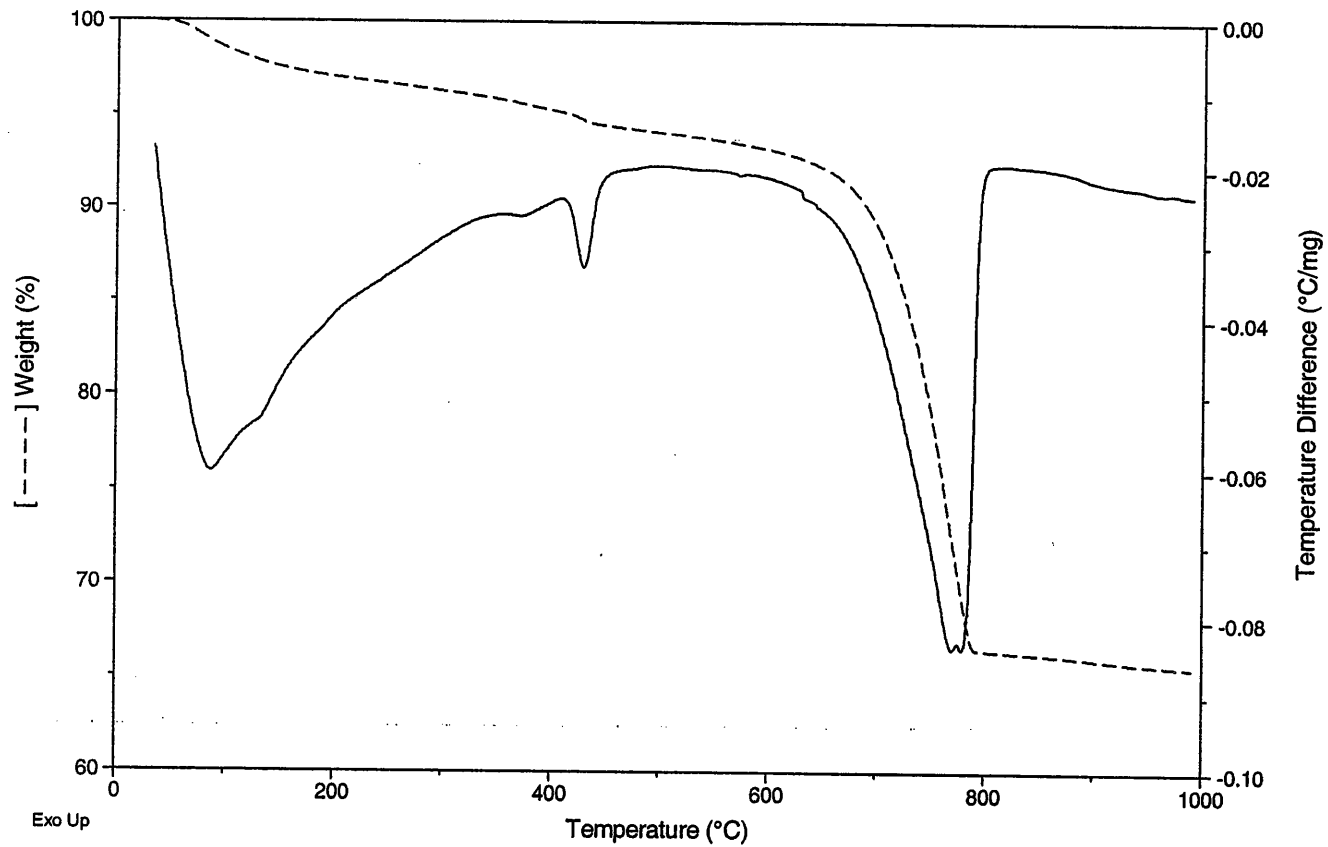


Sample: I70 # 10
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-10.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

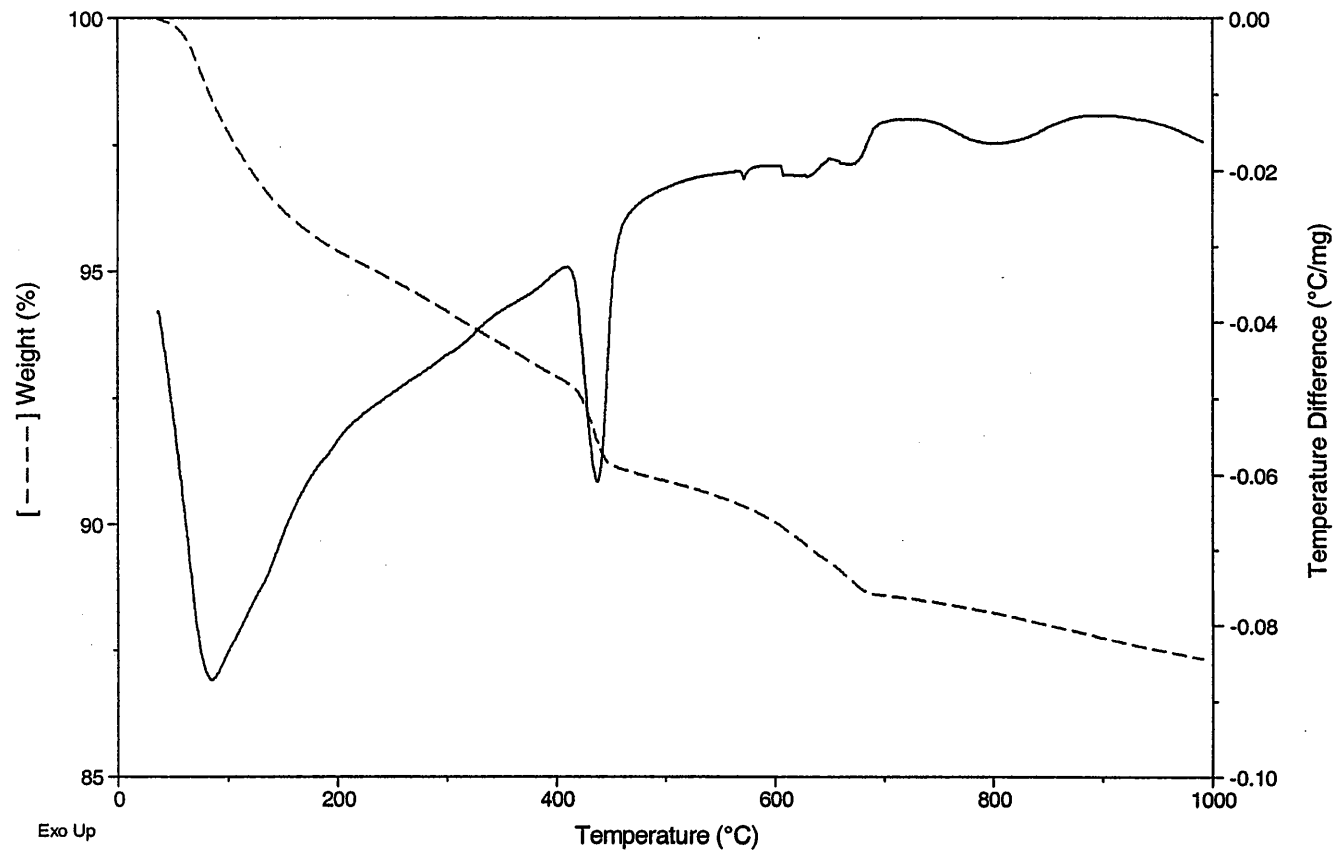


Sample: I70 # 11
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-11.n01
Operator: Supaporn

Comment: Dry N2 100 mL/min

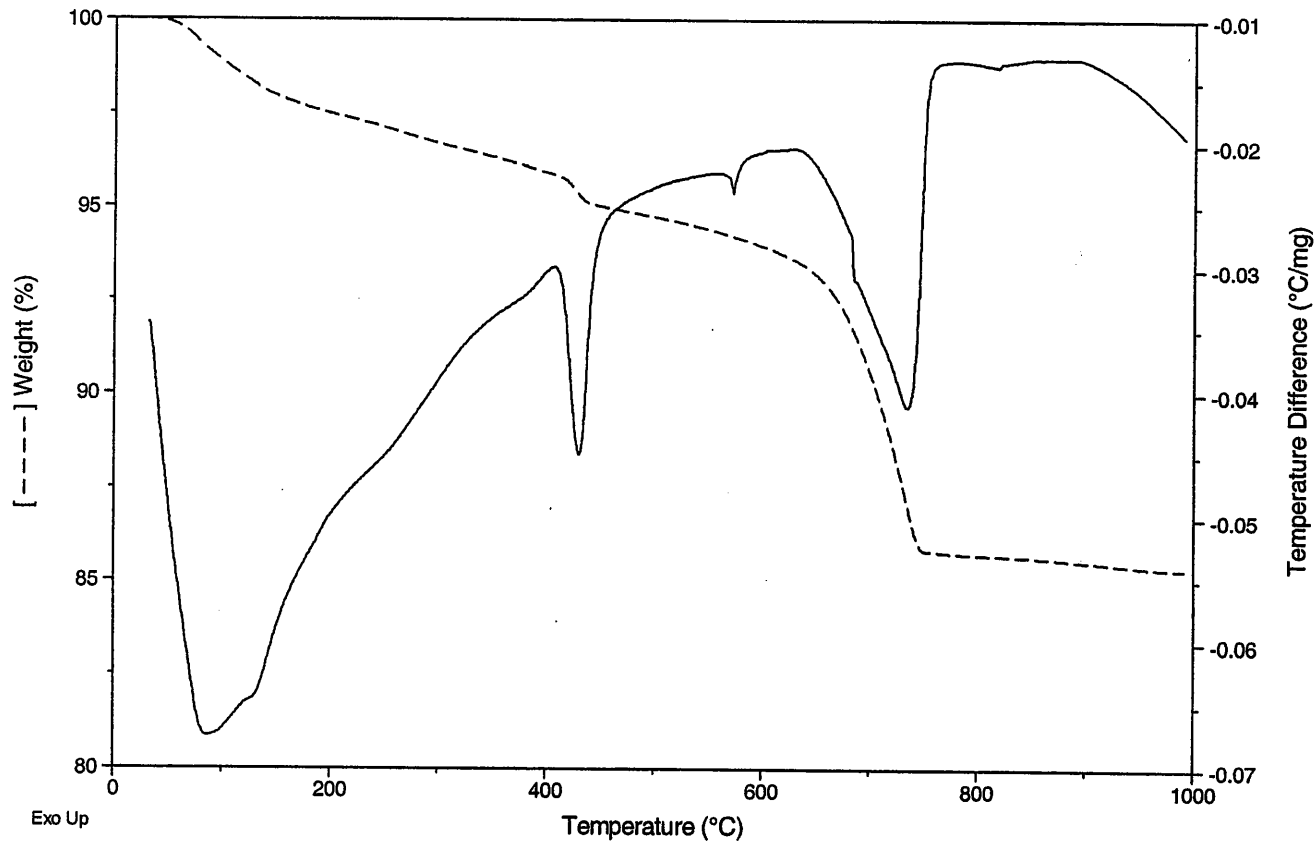


Sample: I70 # 12
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-12.n01
Operator: Supaporn

Comment: Dry N2 100 mL/min

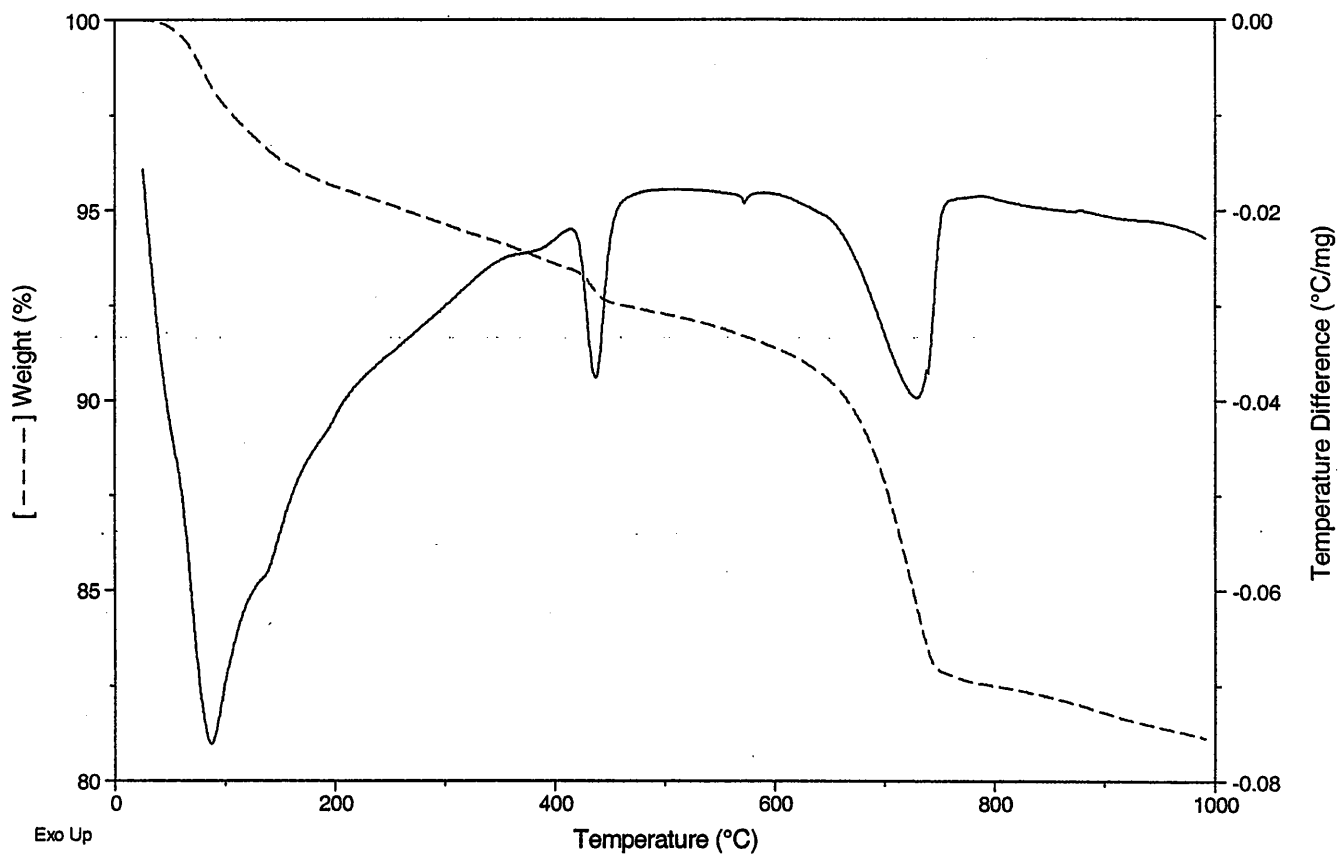


Sample: I70 # 13
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-13.n01
Operator: Supaporn

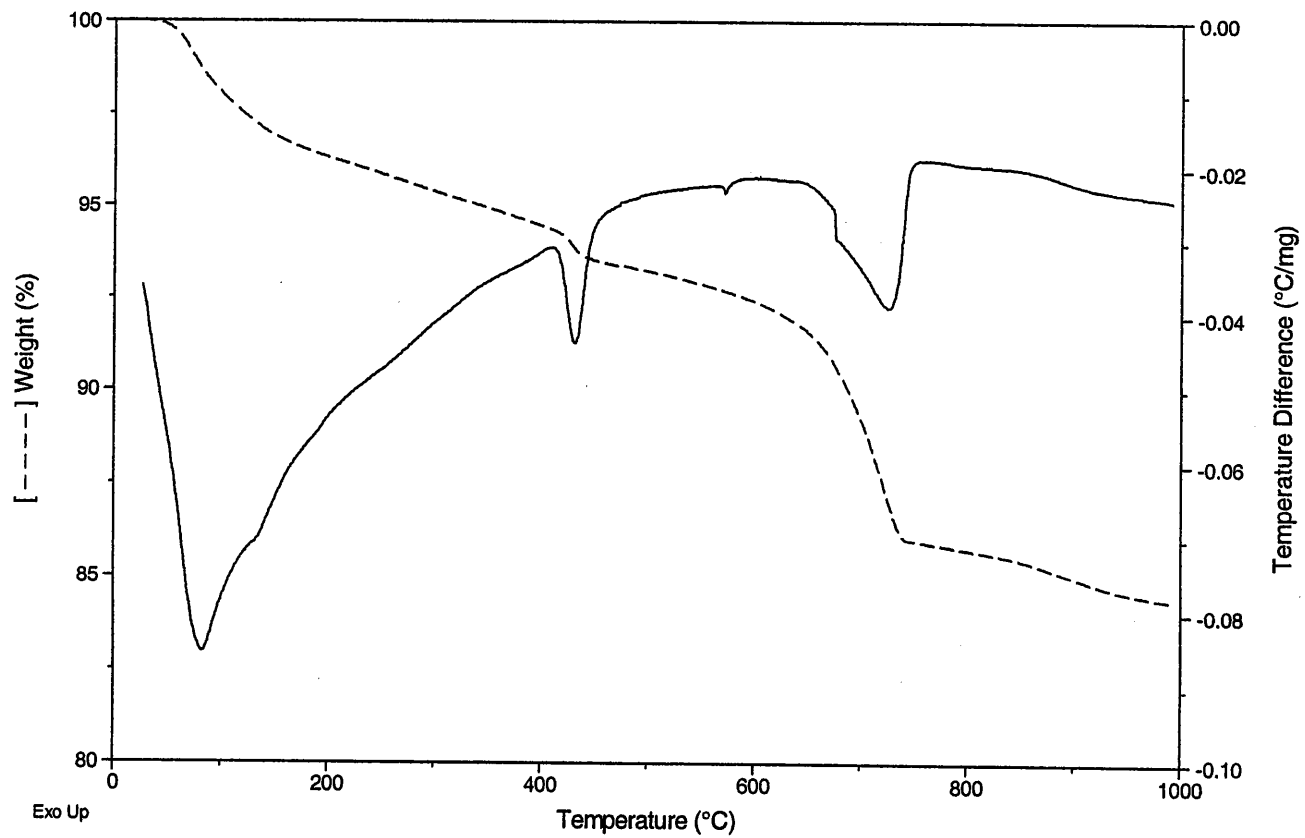
Comment: Dry N2, 100 mL/min



Sample: I70 # 14
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I70-14.n01
Operator: Supaporn

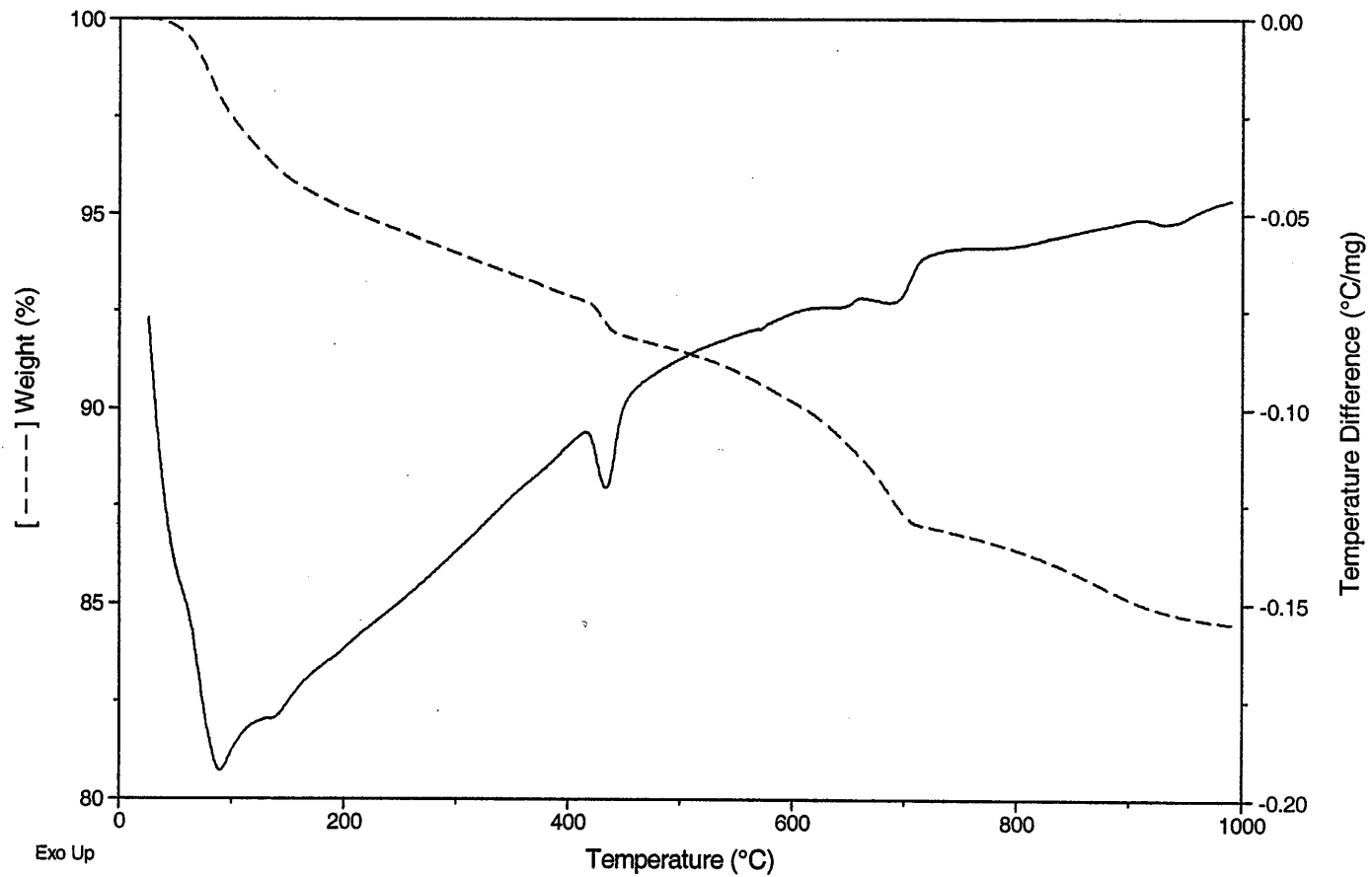


Sample: I70 # 15
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I70-15.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

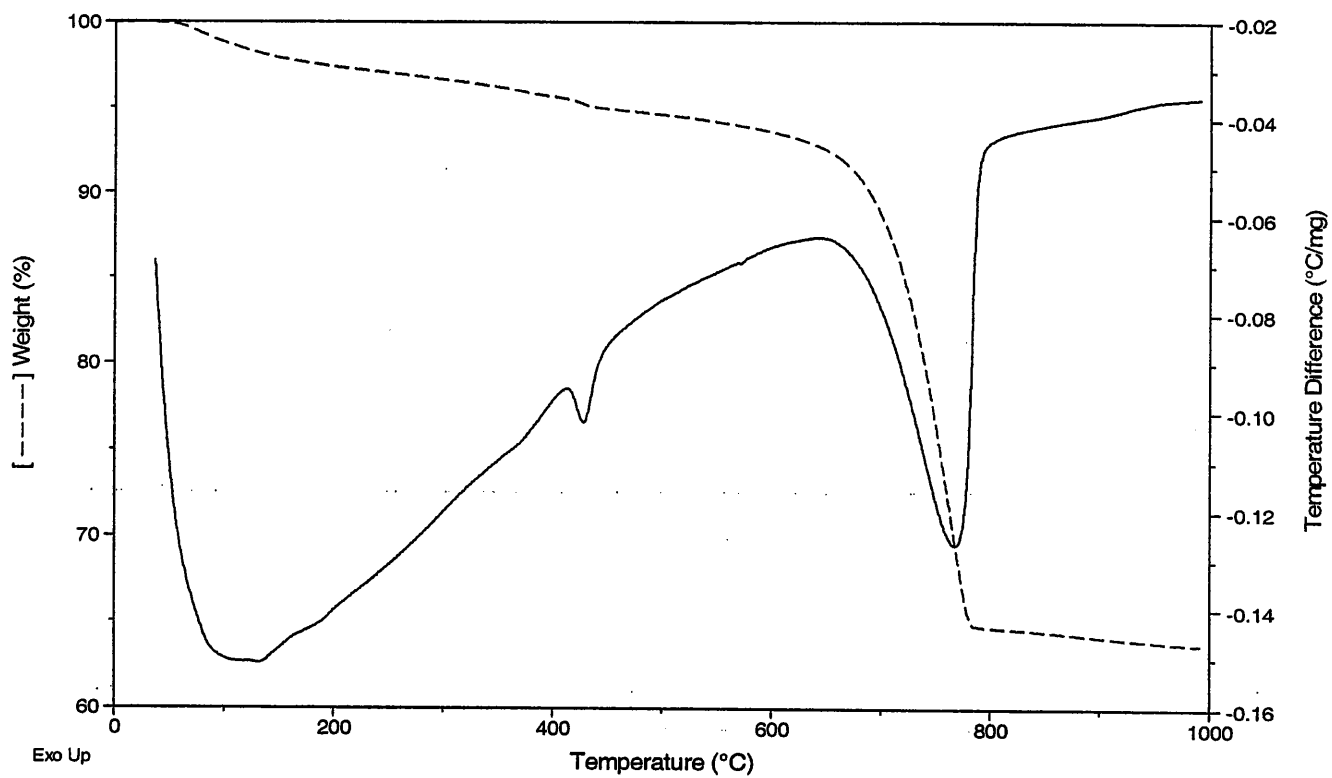


Sample: I70 # 16
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I70-16.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

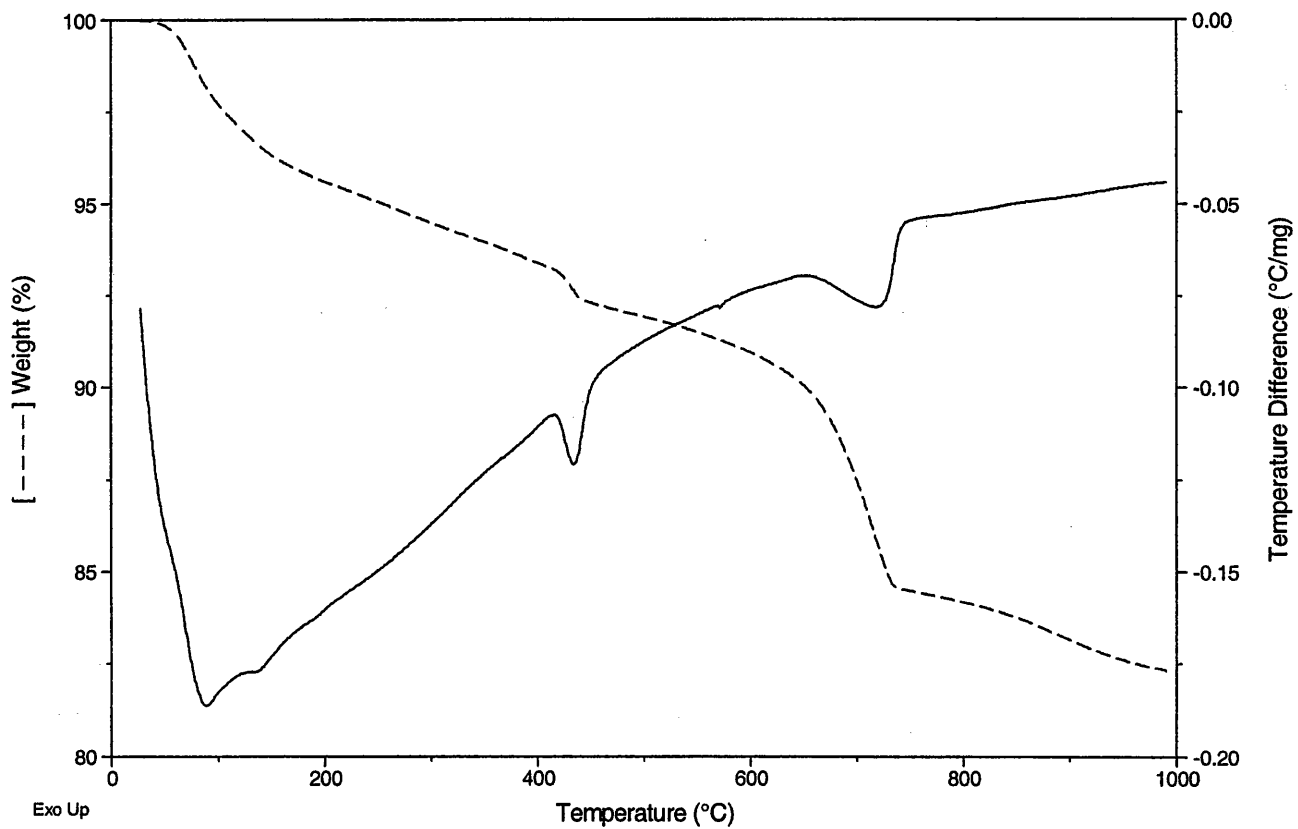


Sample: I70 # 17
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I70-17.n01
Operator: Supaporn

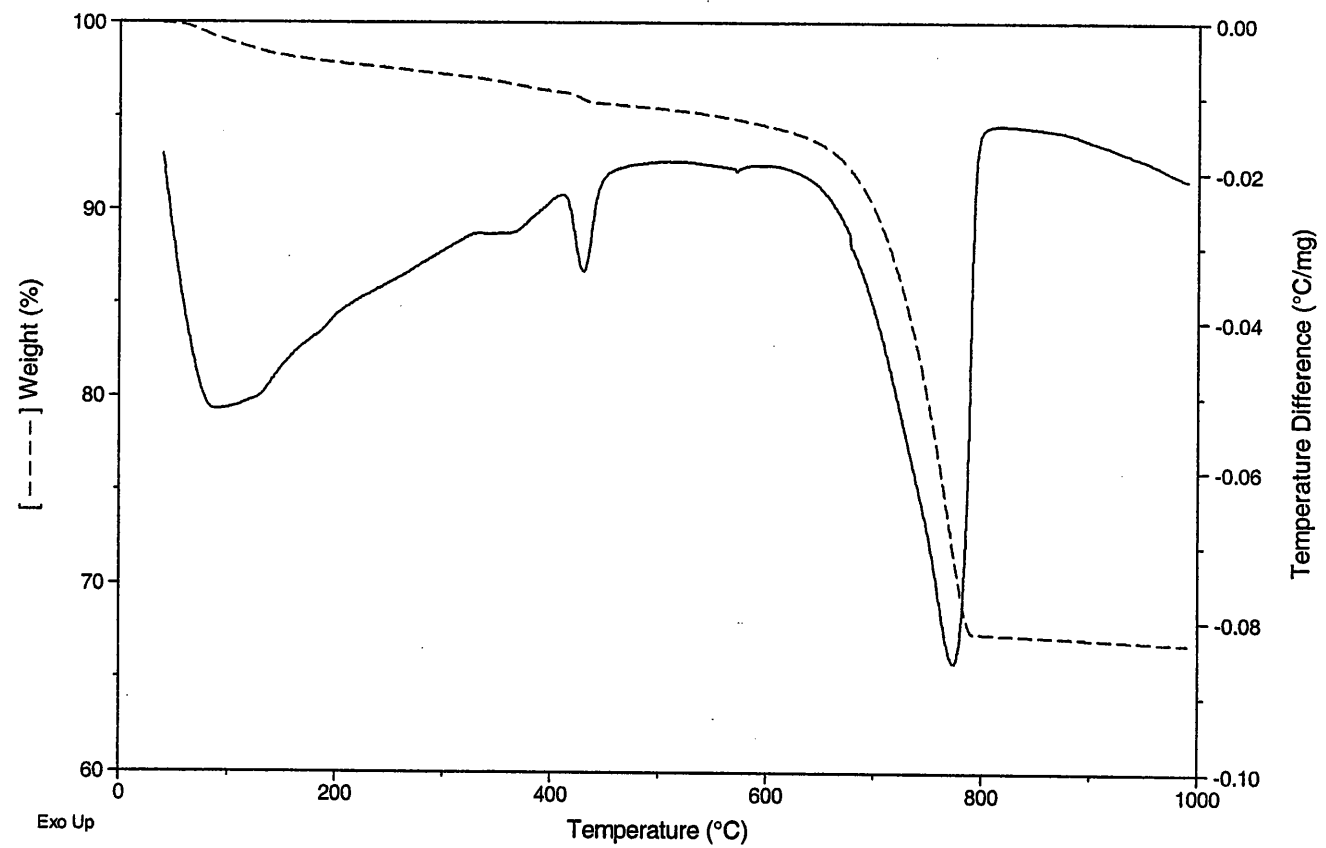
Comment: Dry N2, 100 mL/min



Sample: I71 # 1
Method: 10°C/MIN TO 1000°C
Comment: Dry N2, 100 mL/min

TGA-DTA

File: C:\ODOT\I71-1.n01
Operator: Supaporn

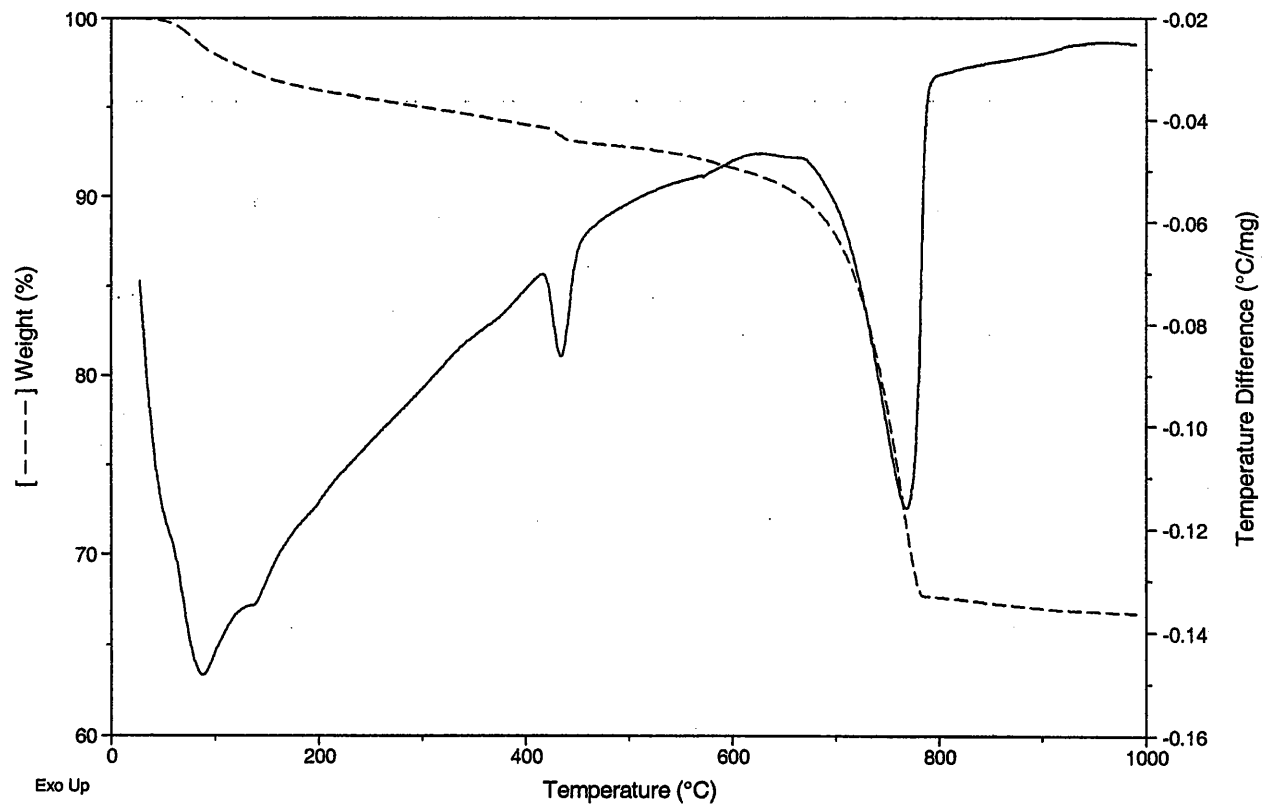


Sample: I71 # 2
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I71-2.n01
Operator: Supaporn

Comment: 10°C/min to 1000°C, Dry N2; 100 mL/min

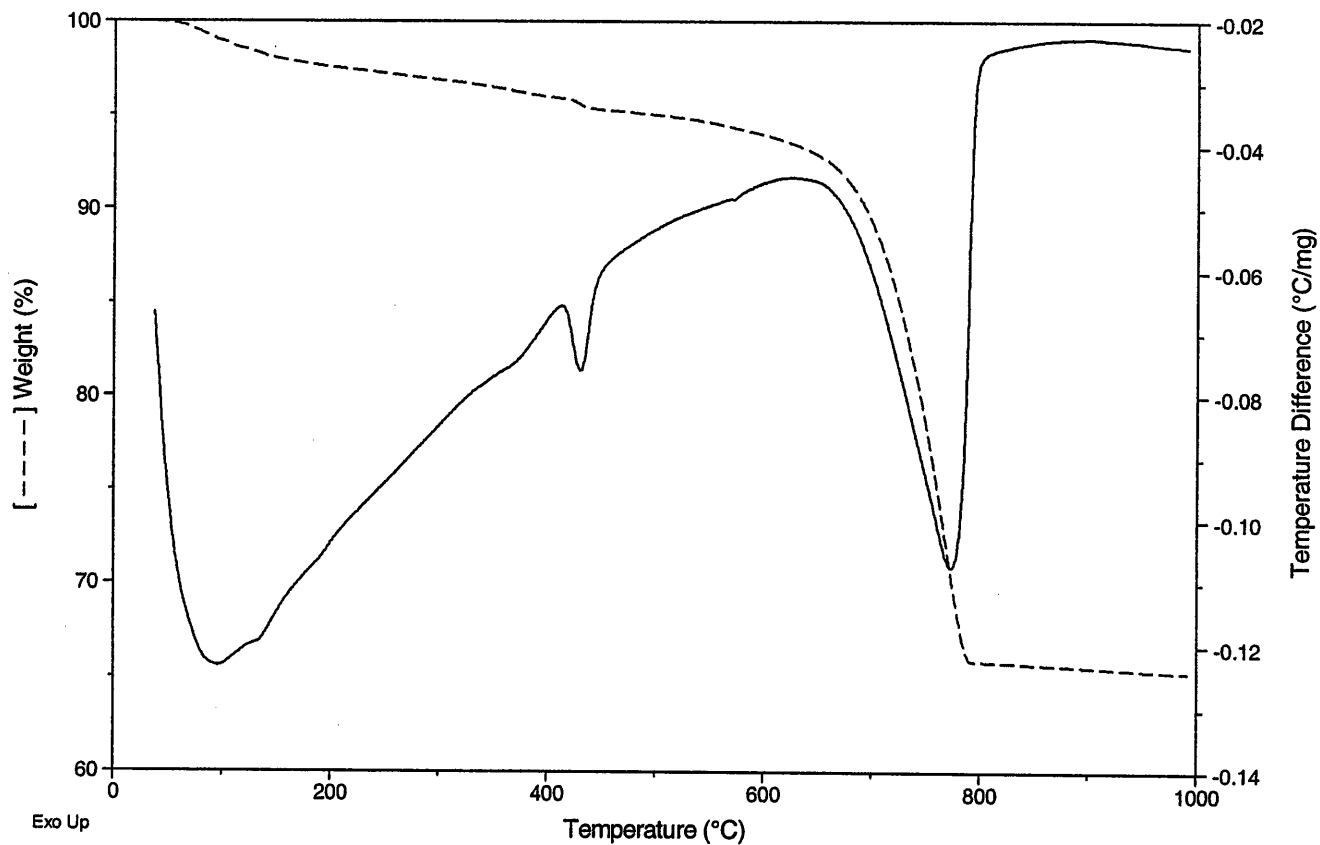


Sample: I71 #3
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I71-3.n01
Operator: Supaporn

Comment: Dry N2; 100 mL/min

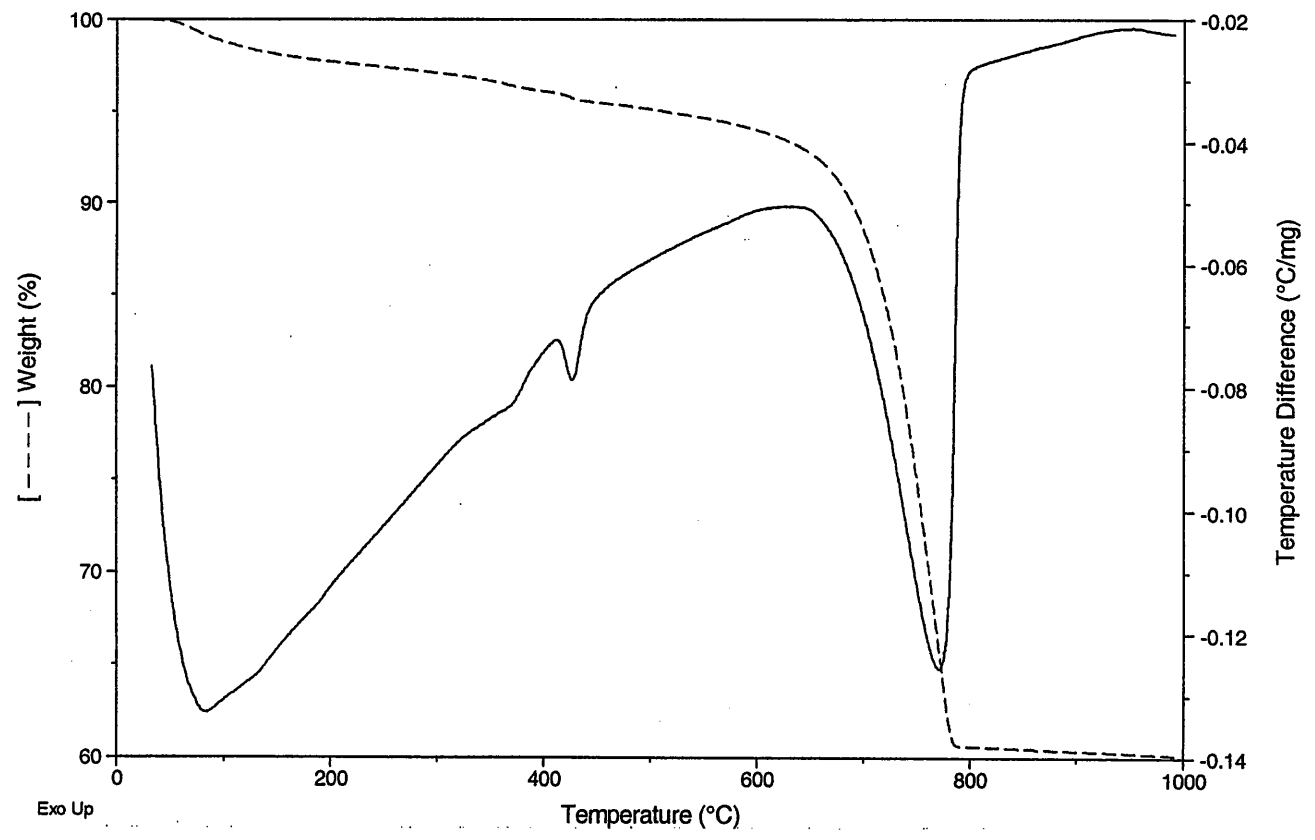


Sample: I71 # 4
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I71-4.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

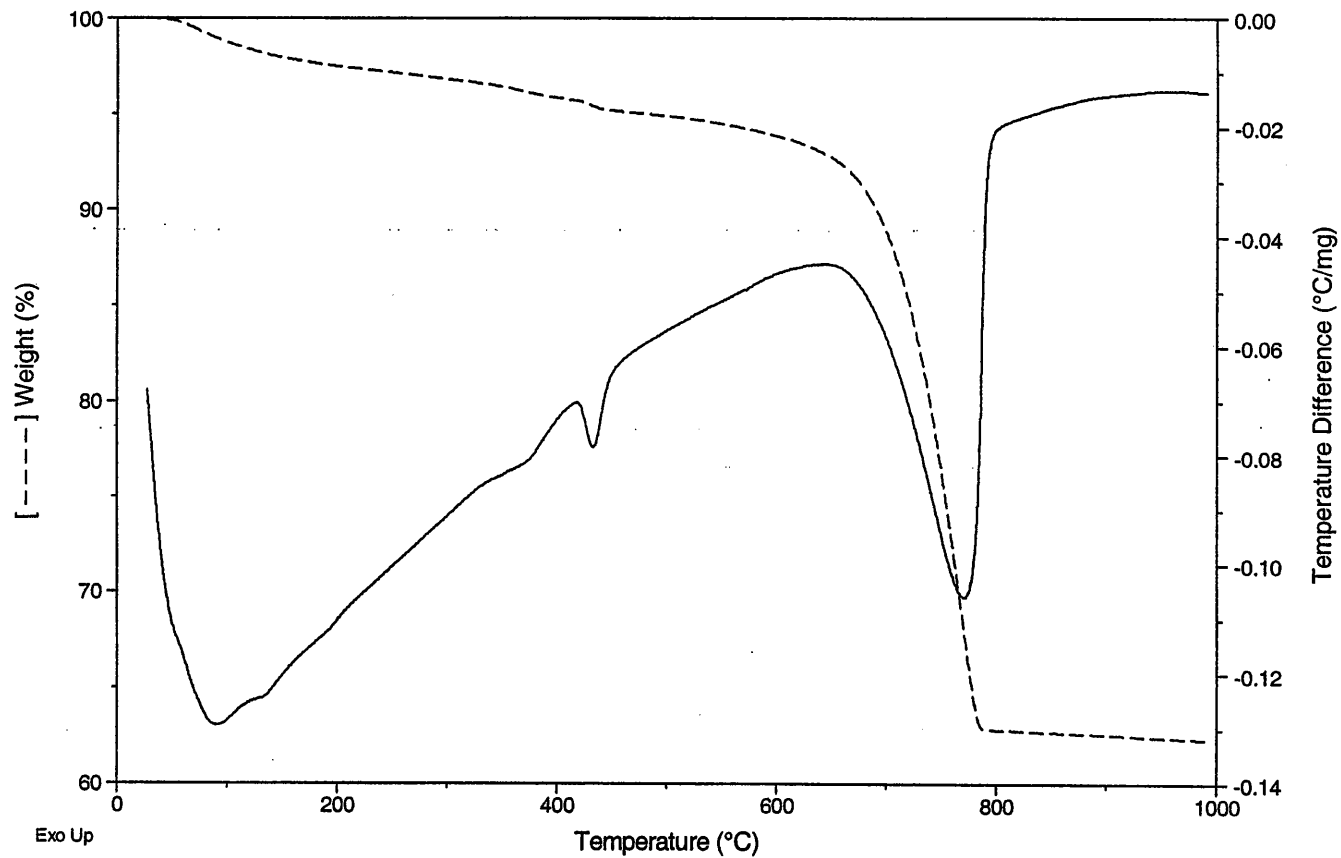


Sample: I71 # 5
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I71-5.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

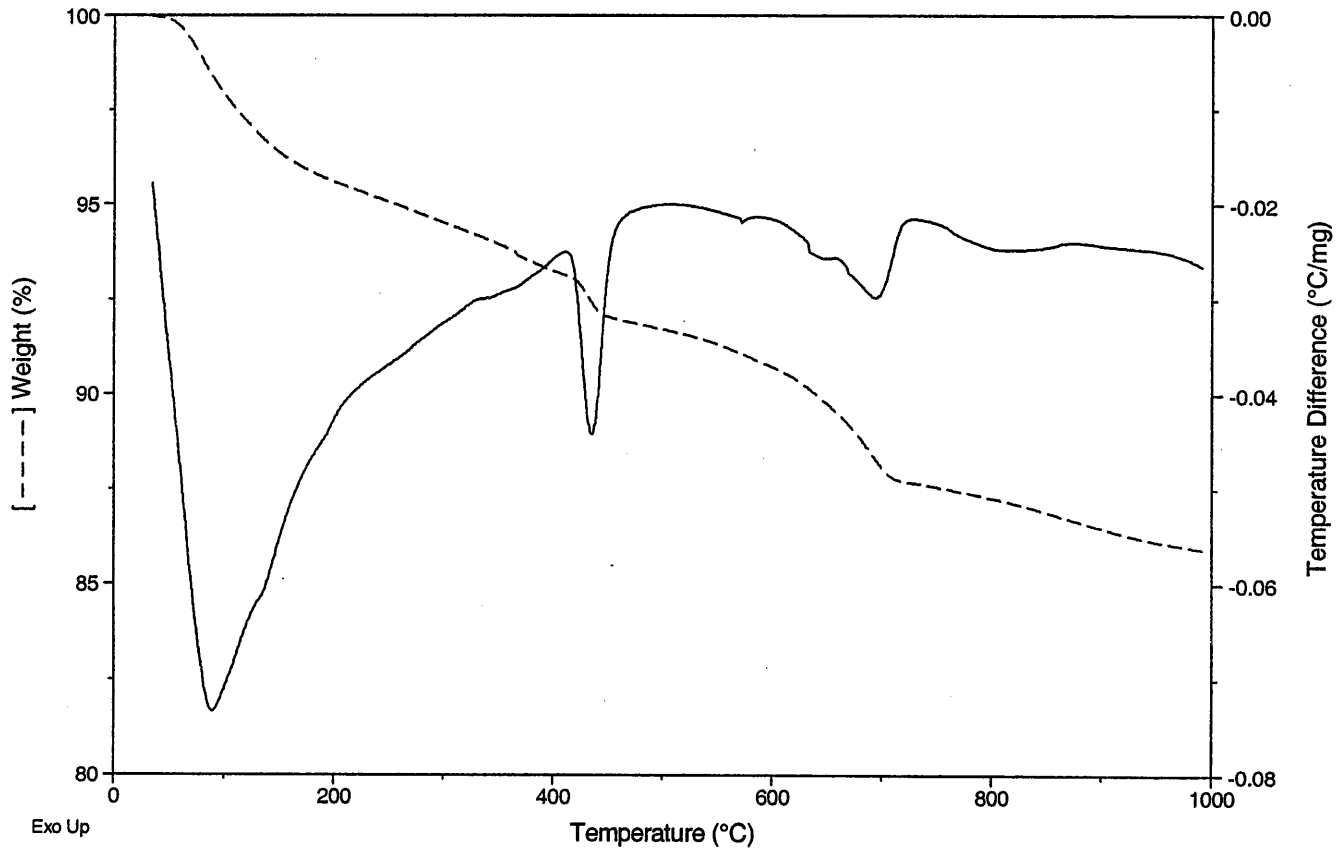


Sample: I71 # 6
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I71-6.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

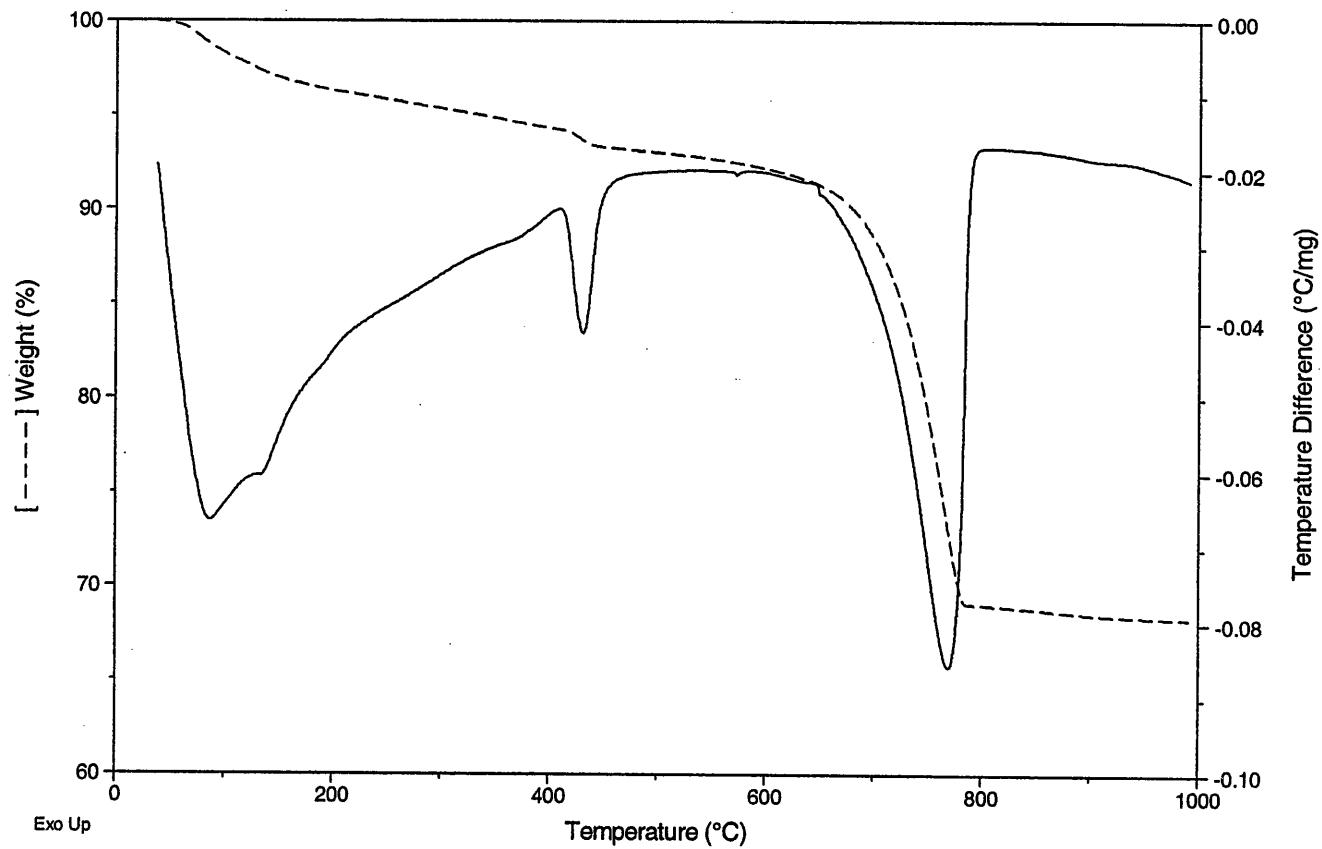


Sample: I71 #7
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I71-7.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

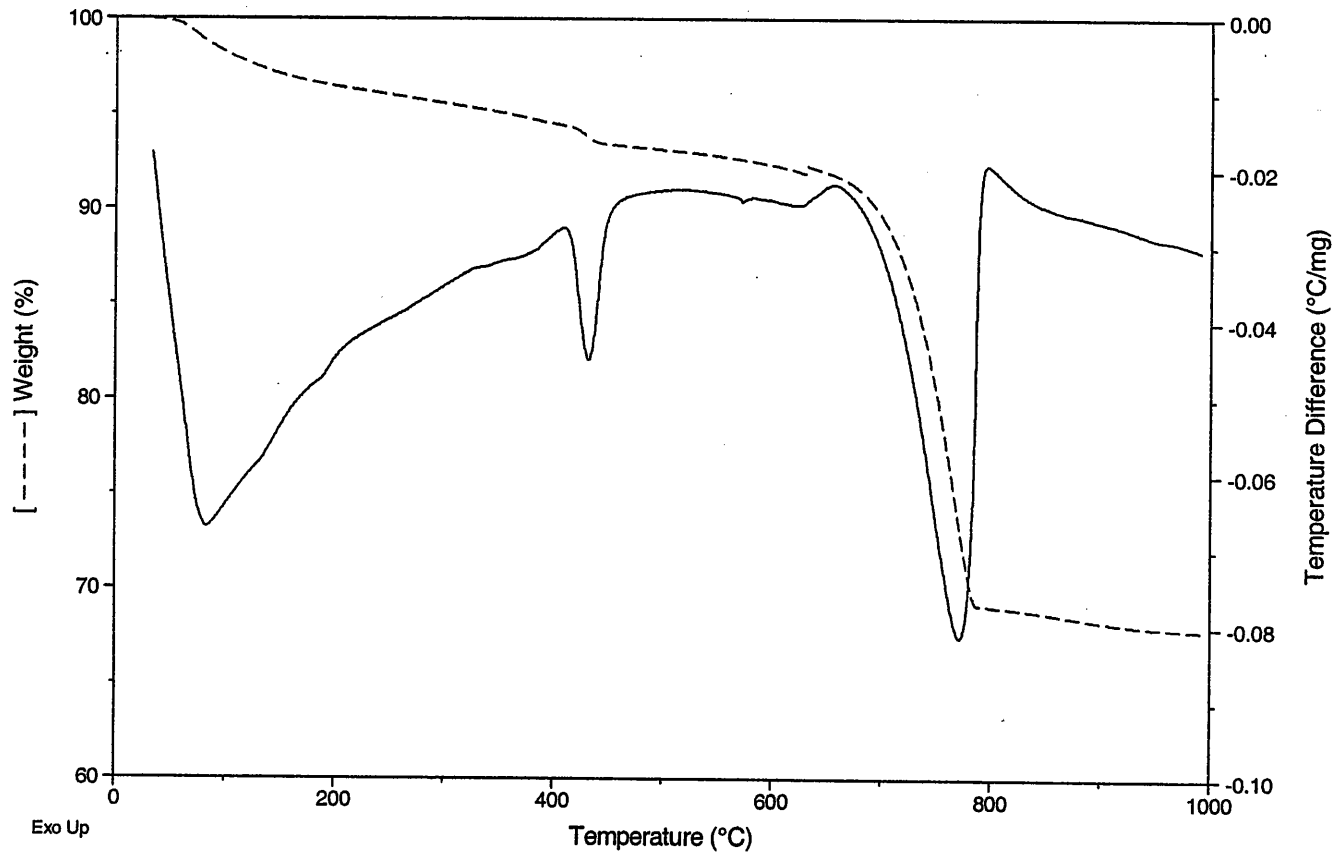


Sample: I71 # 8
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I71-8.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

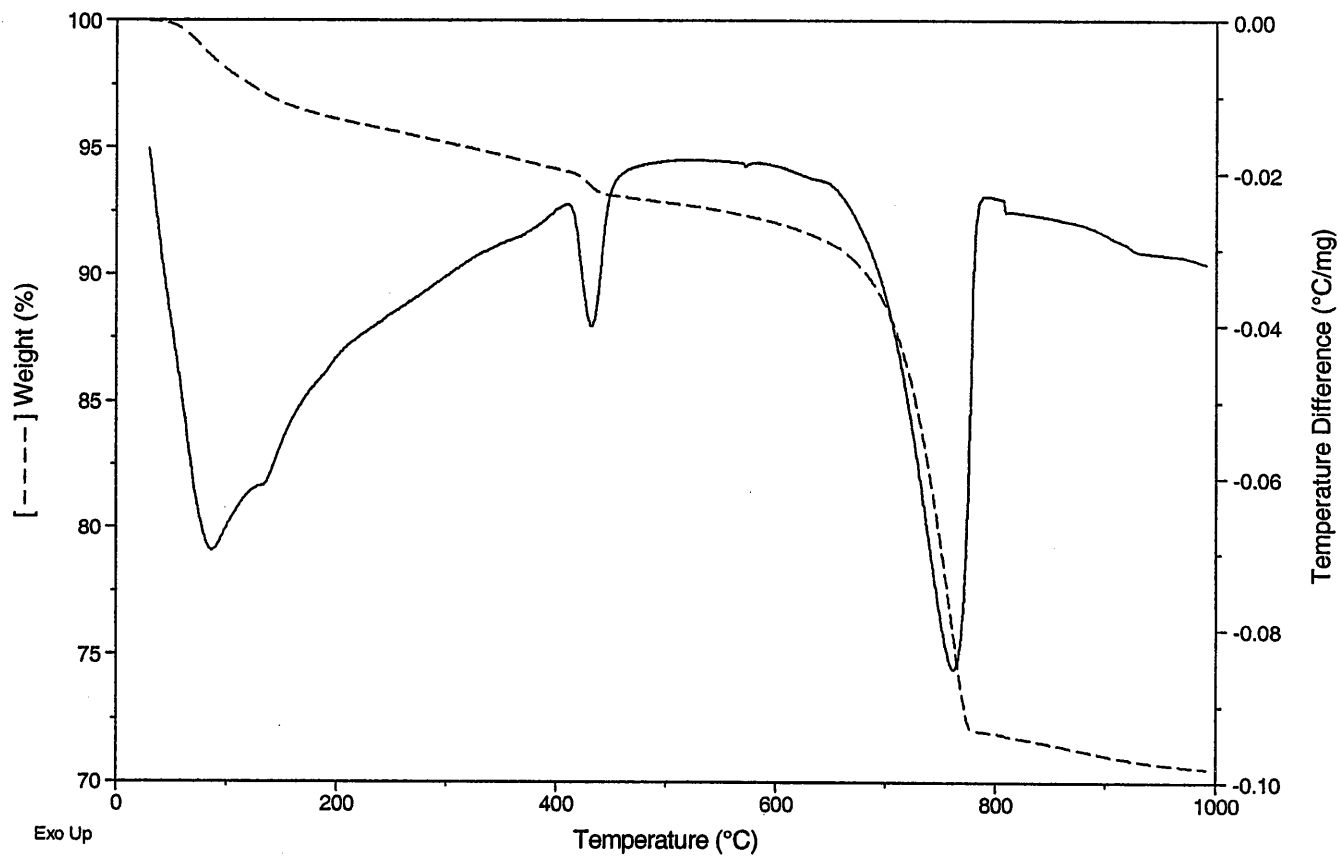


Sample: I71 # 9
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I71-9.n01
Operator: Supaporn

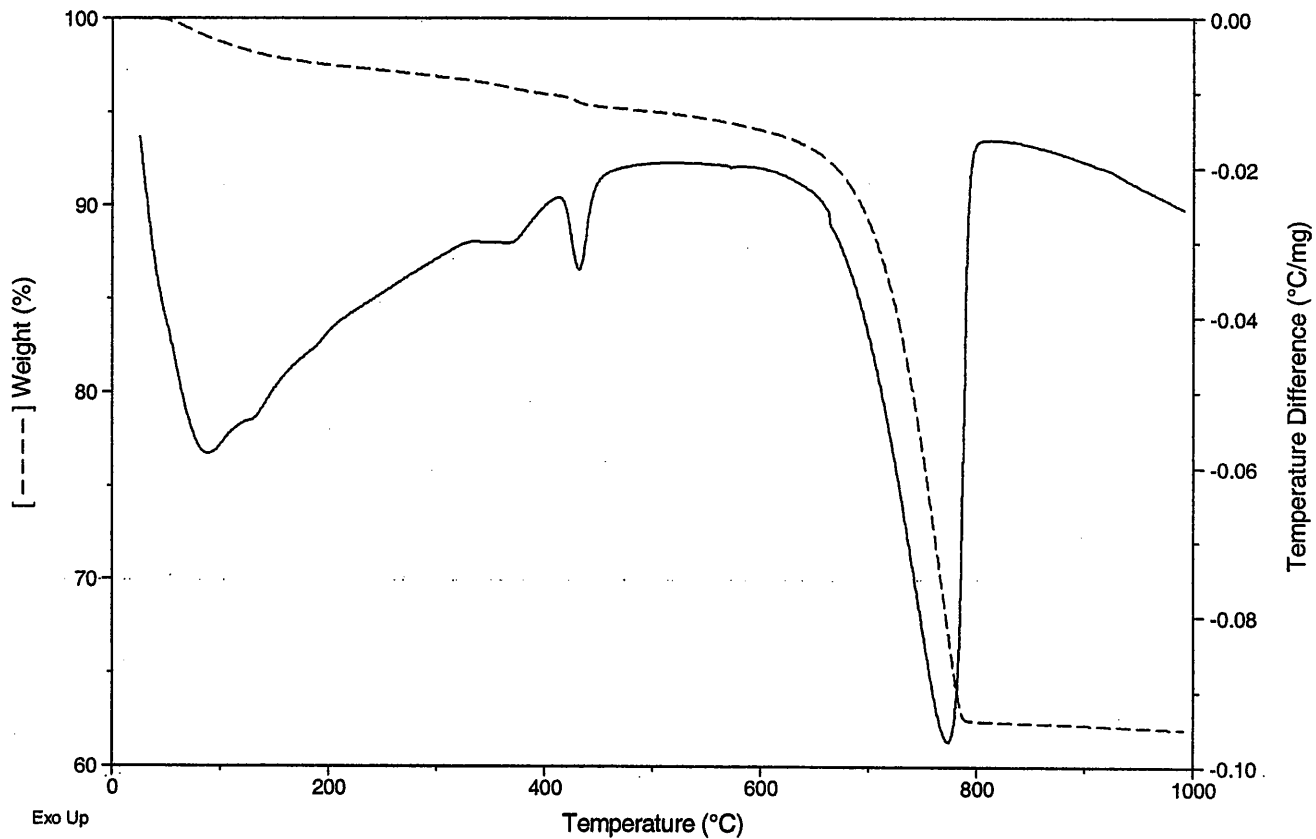
Comment: Dry N2, 100 mL/min



Sample: I75 # 3
Method: 10°C/MIN TO 1000°C
Comment: Dry N2, 100 mL/min

TGA-DTA

File: C:\ODOT\I75-3.n01
Operator: Supaporn

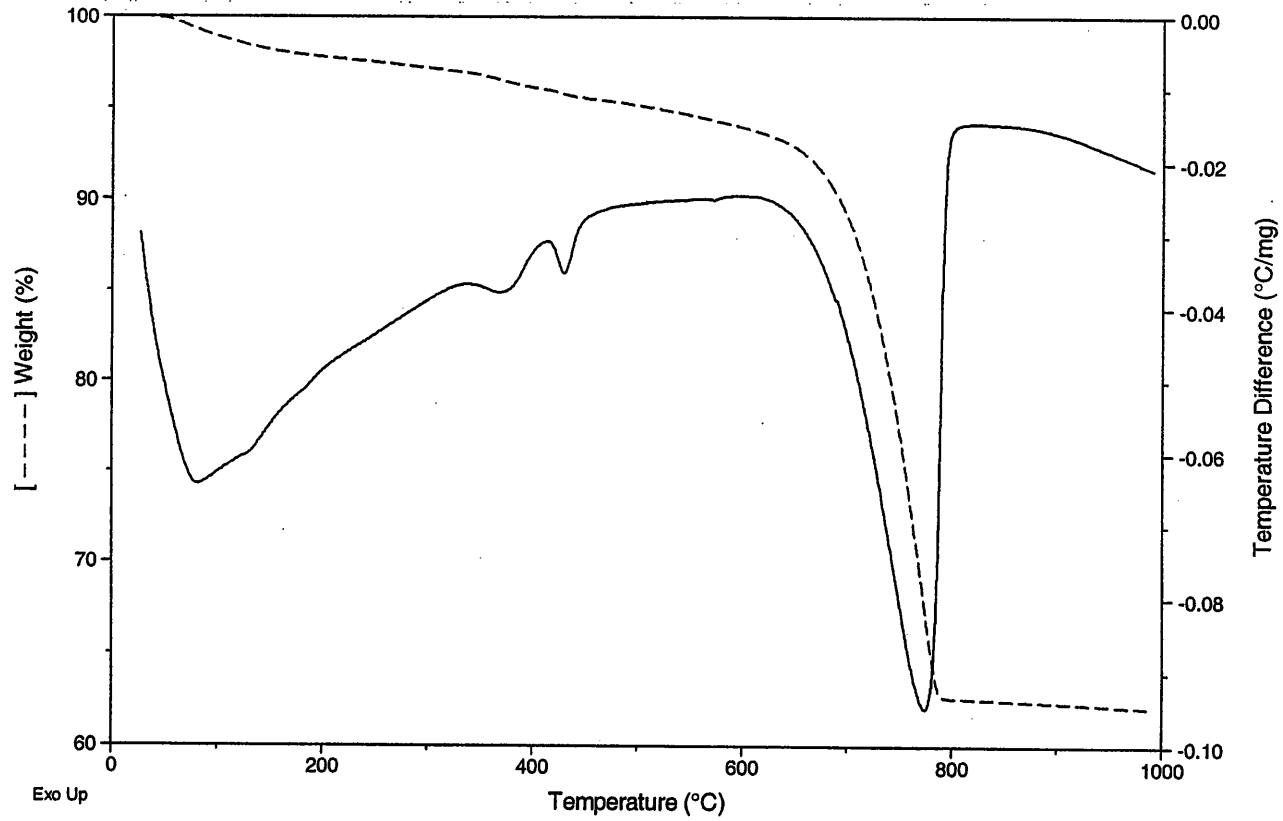


Sample: I-75 # 5
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I75-5.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

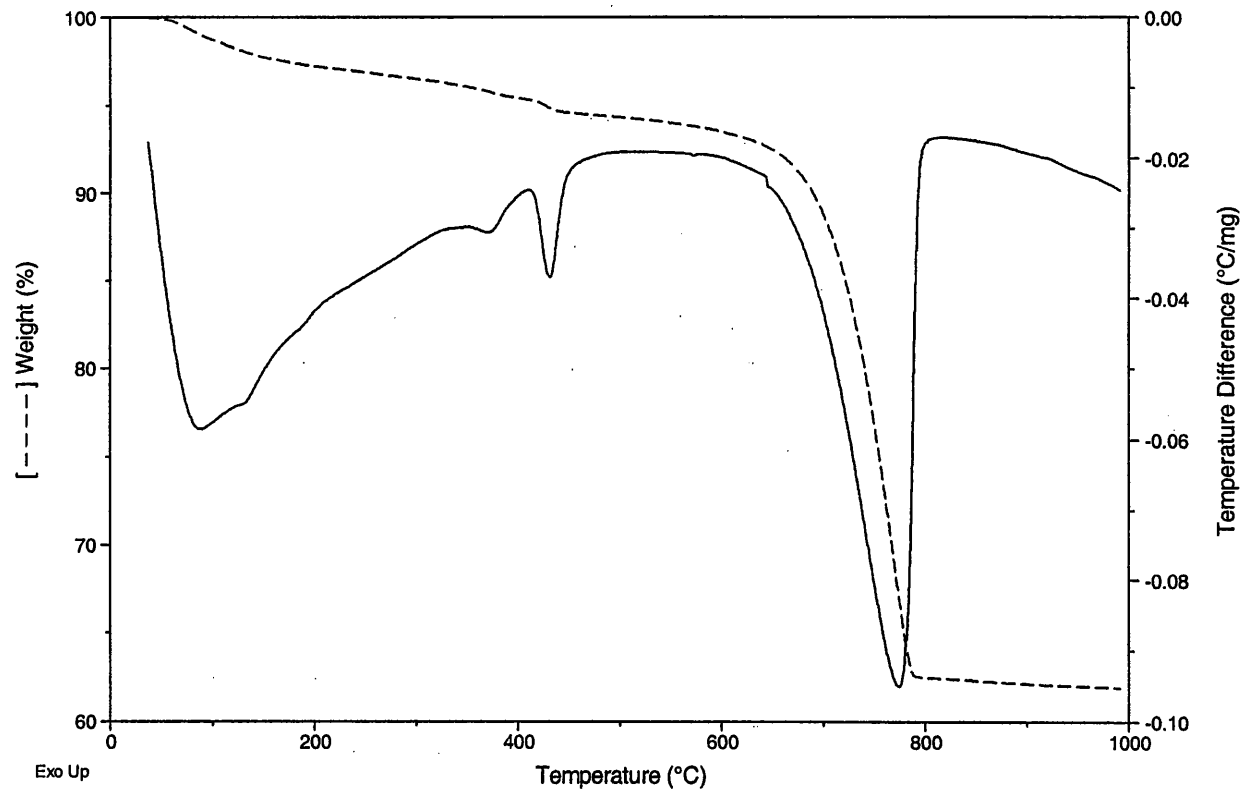


Sample: I75 # 6
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I75-6.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

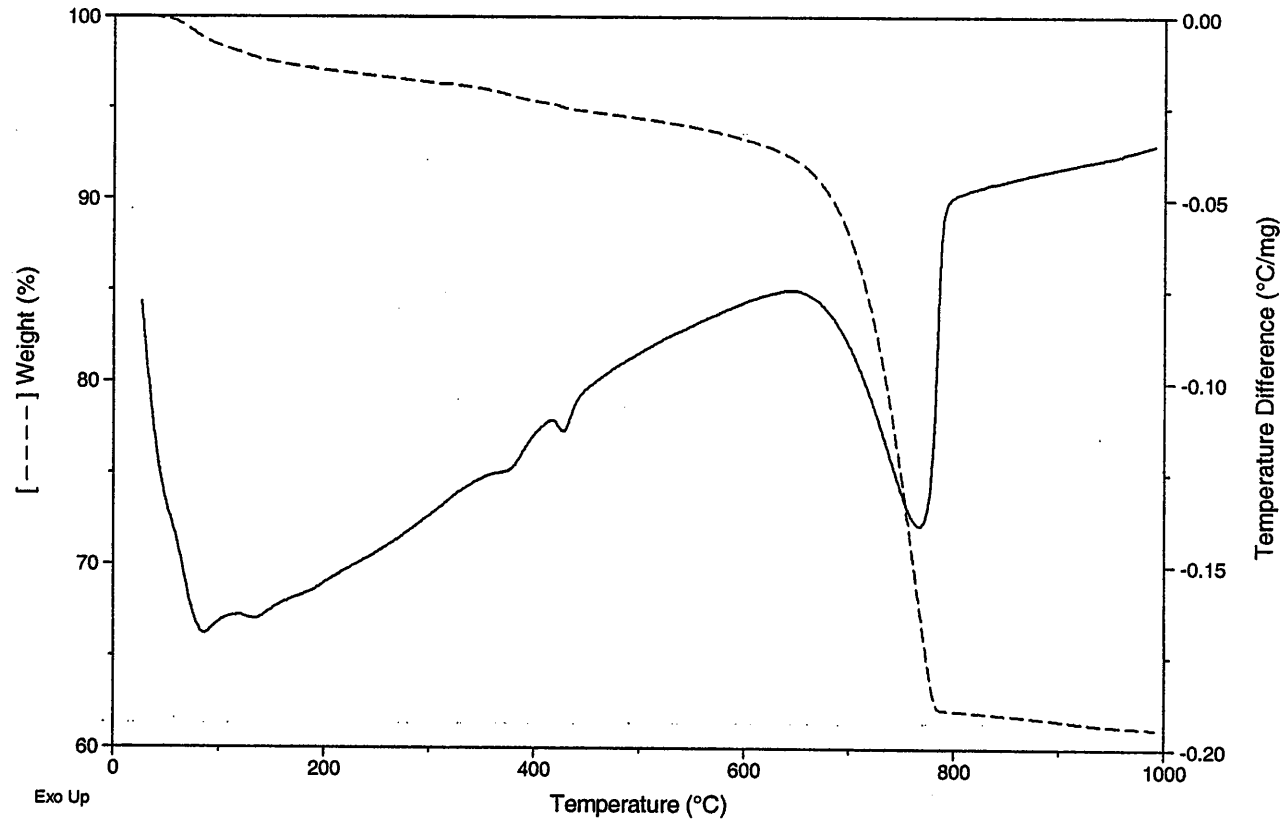


Sample: I75 # 7
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I75-7.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

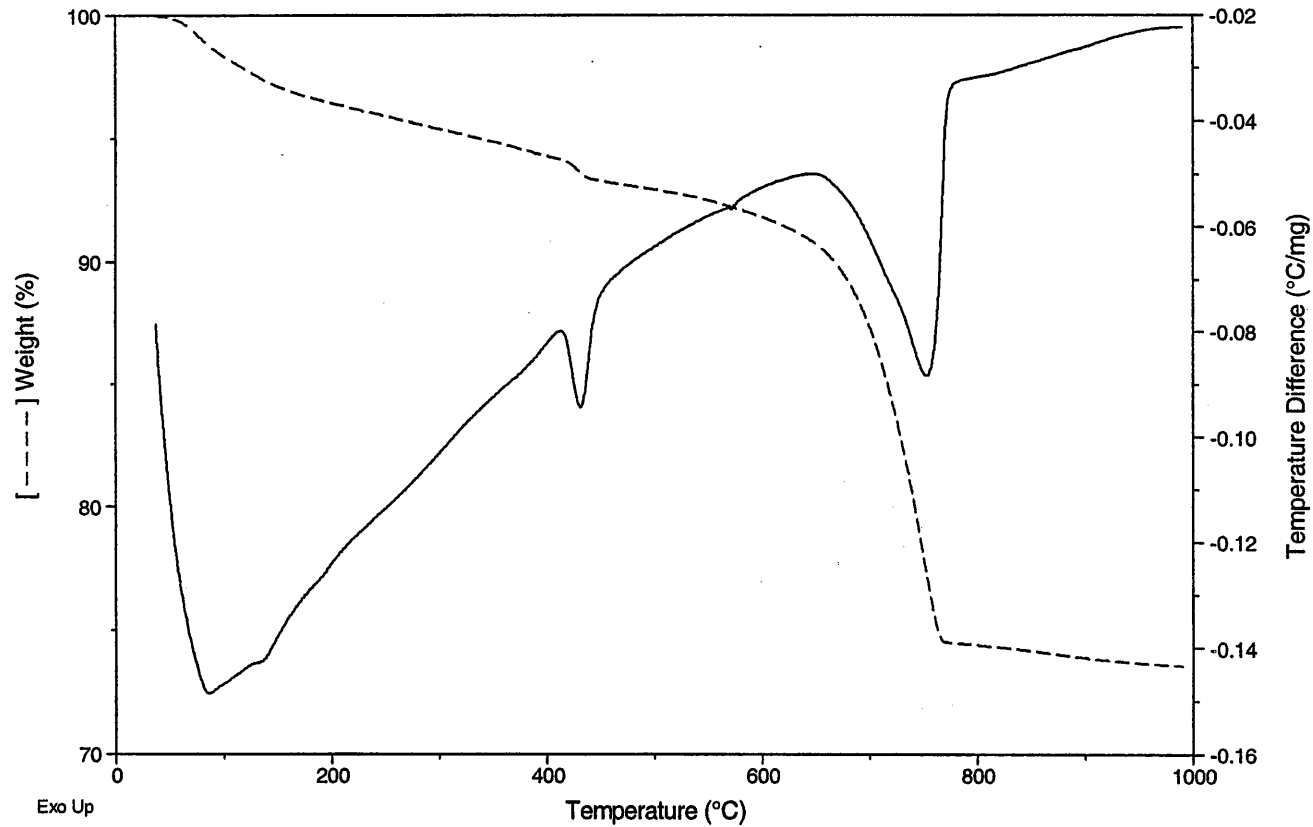


Sample: I77 # 1
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I77-1.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

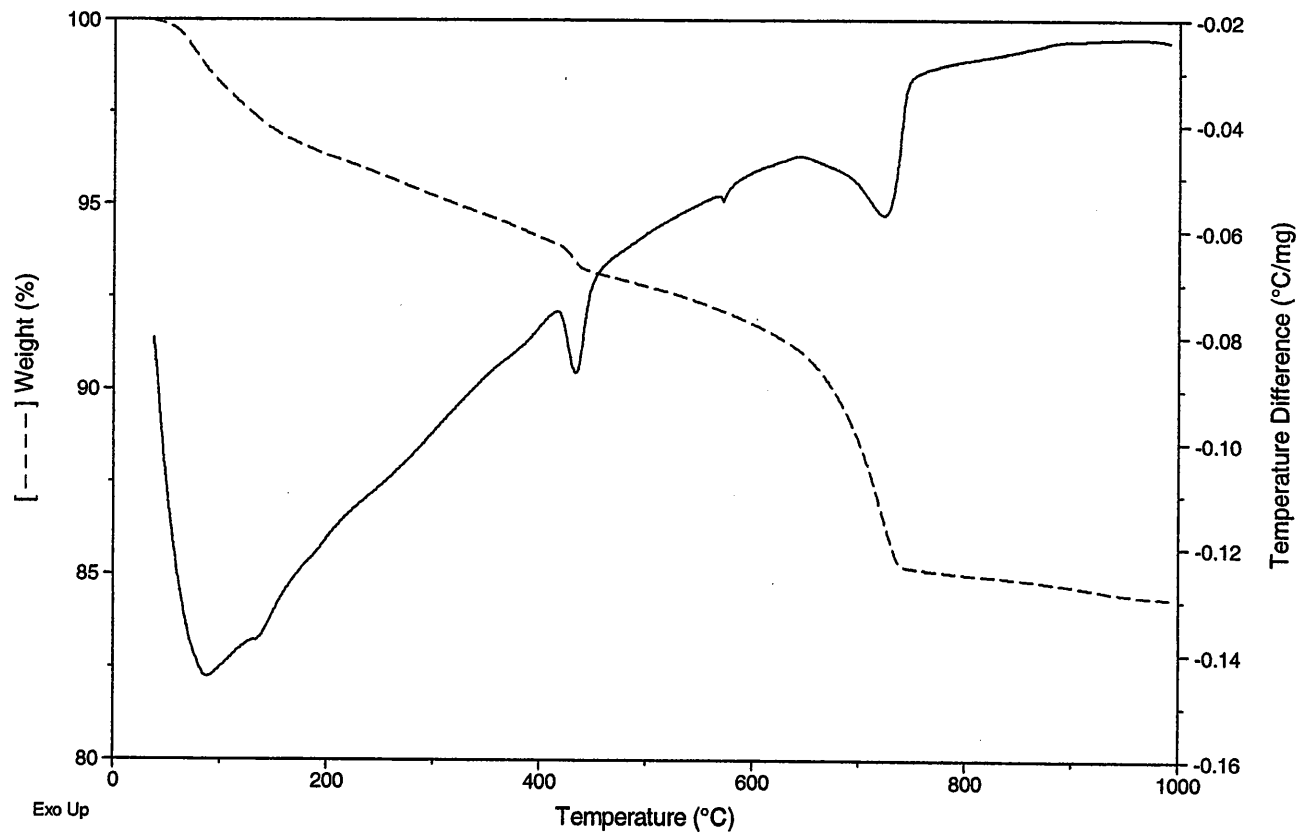


Sample: I77 # 2
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I77-2.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

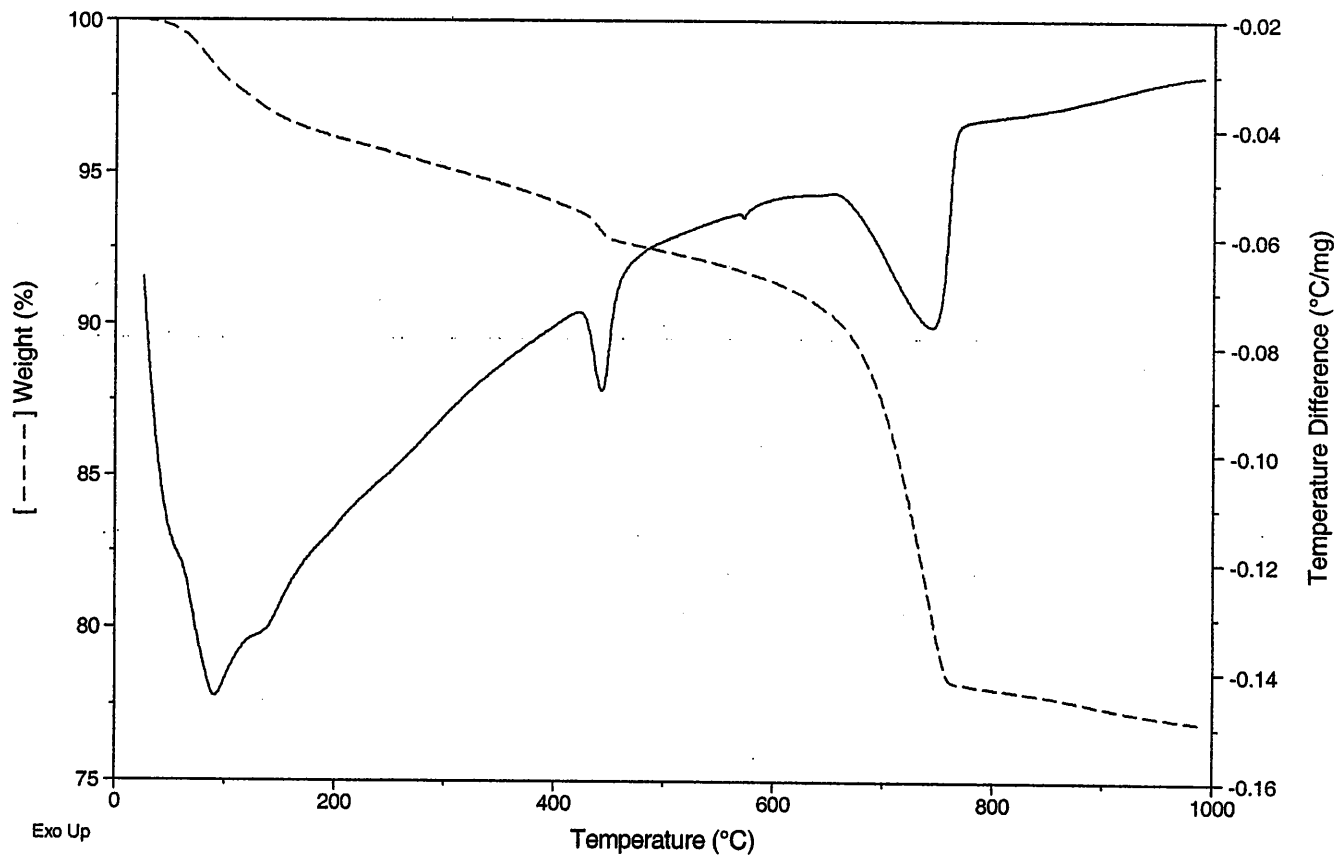


Sample: I77 # 3
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I77-3.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

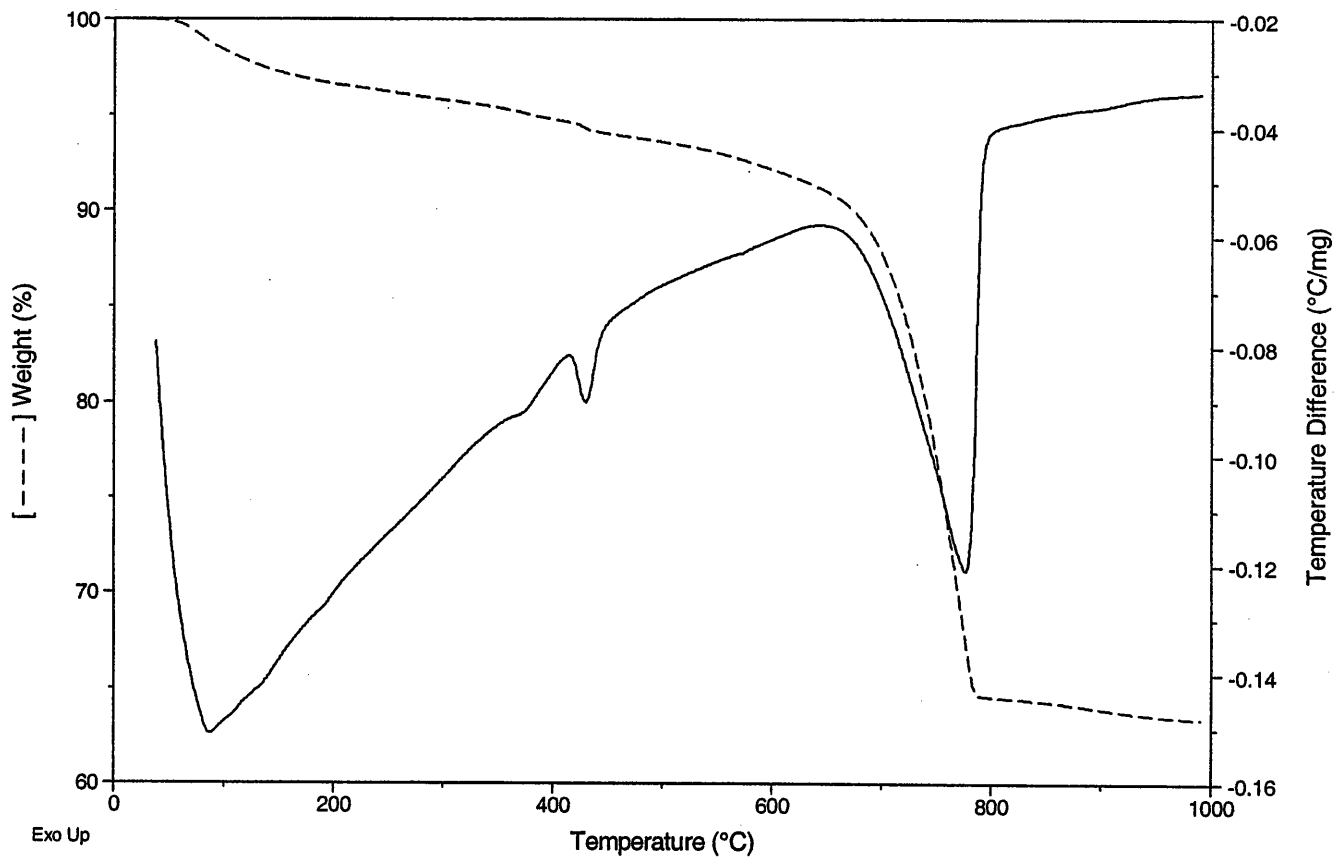


Sample: I77 # 4
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I77-4.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

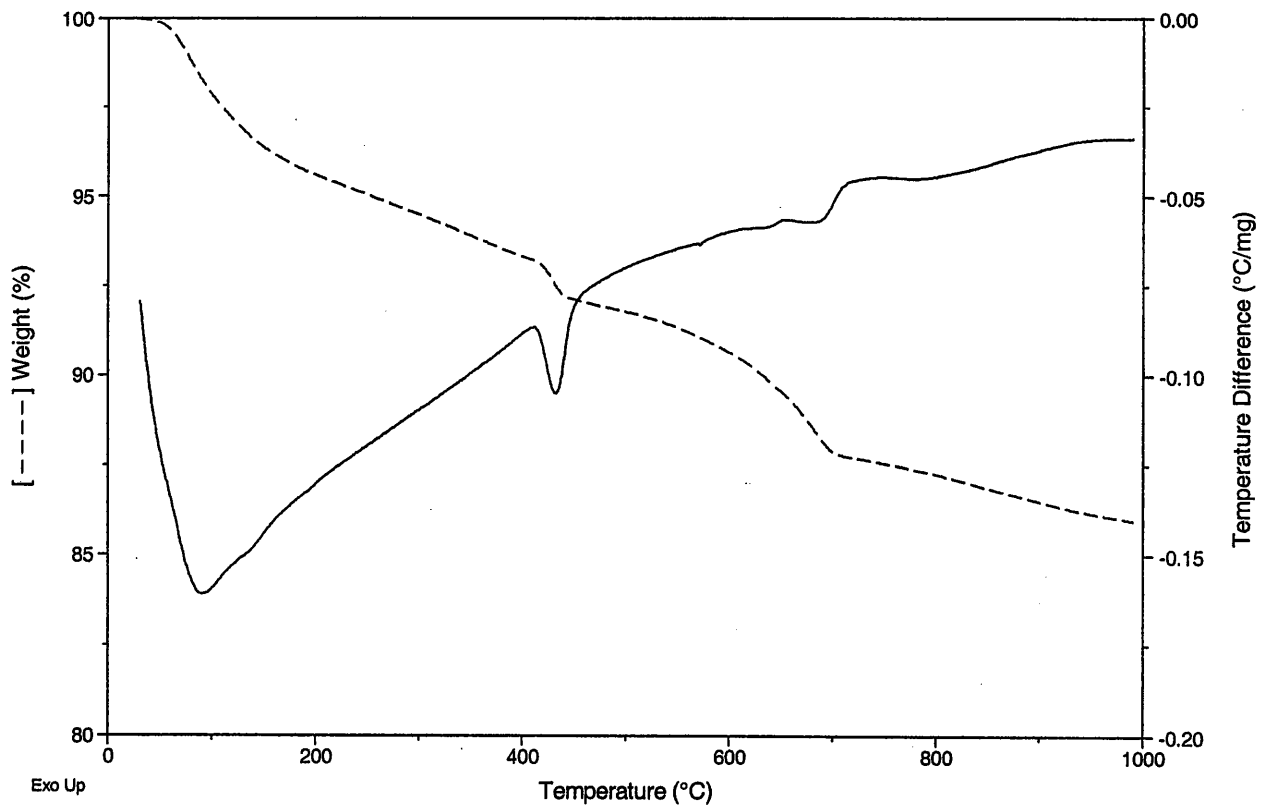


Sample: I77 # 5
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I77-5.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

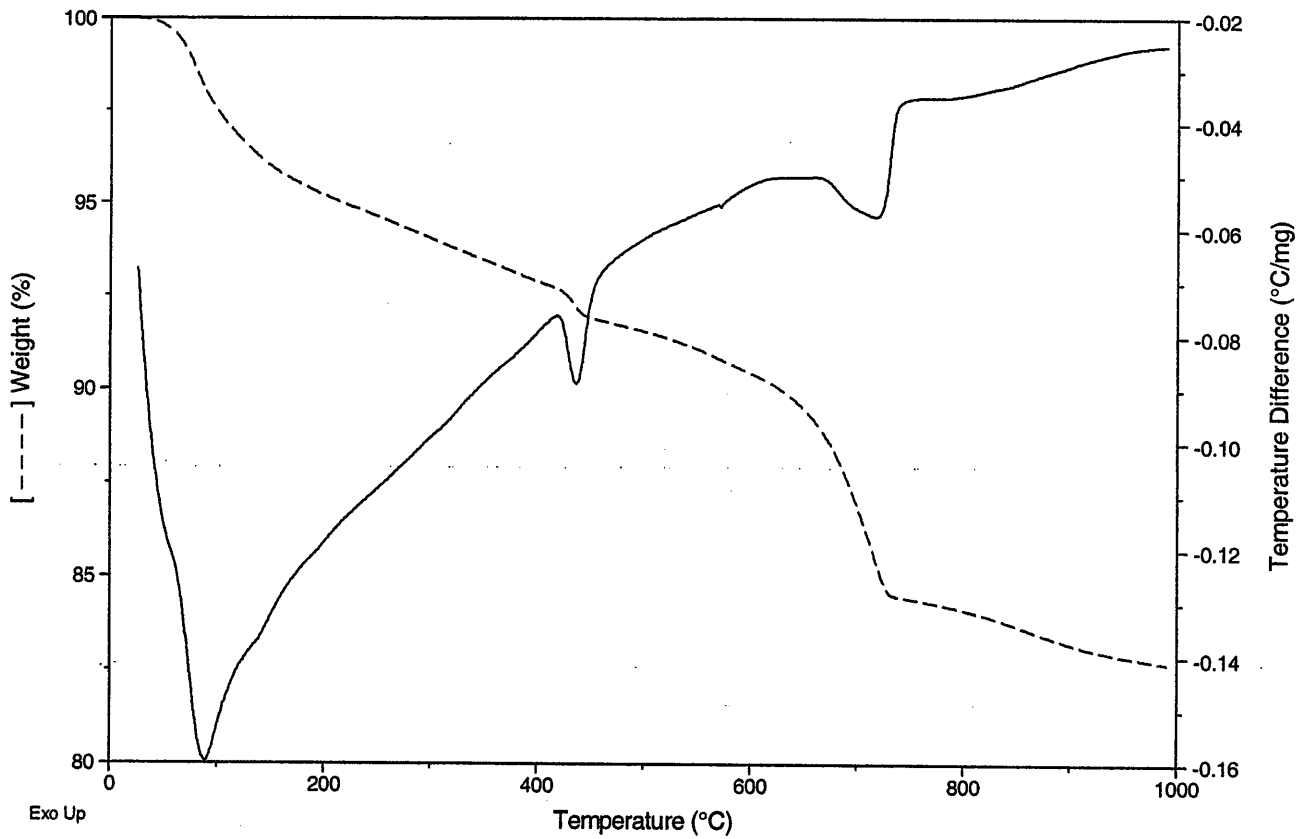


Sample: I77 # 6
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I77-6.n01
Operator: Supaporn

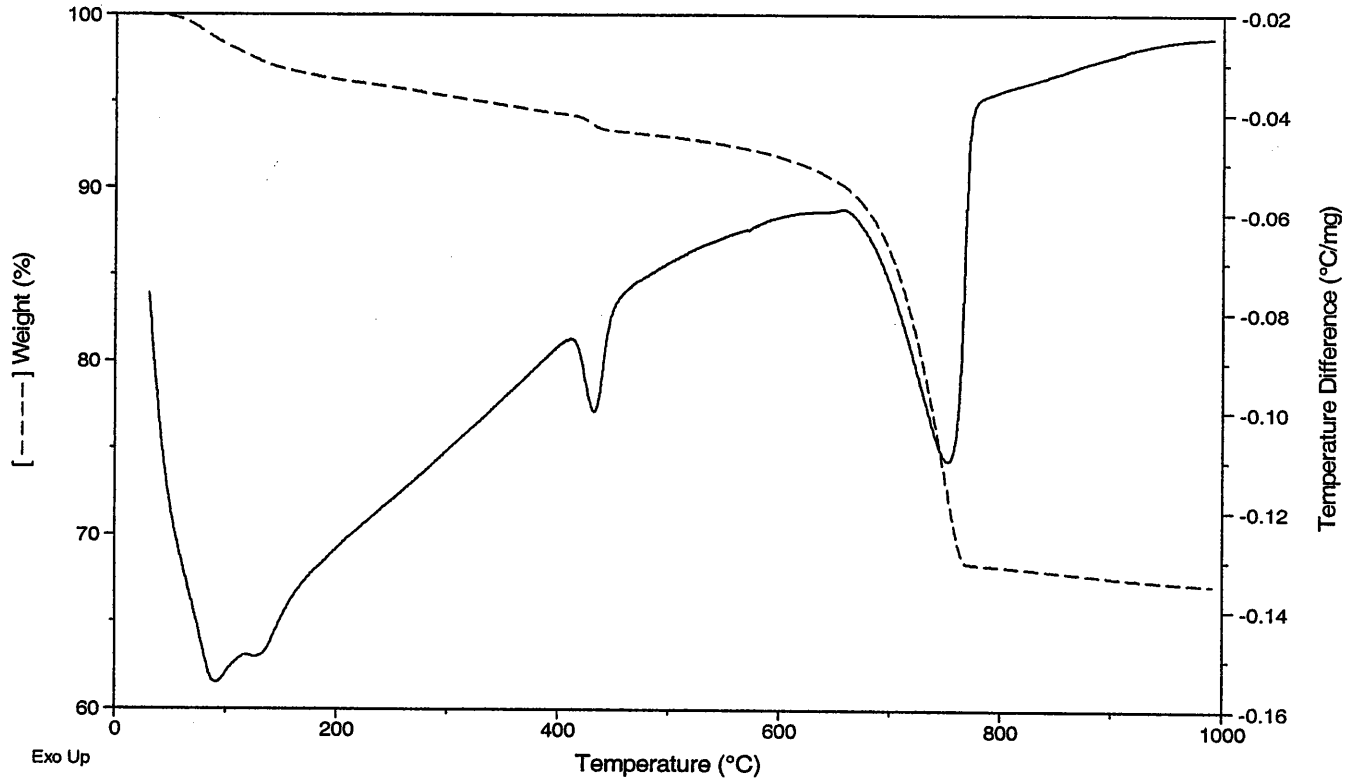
Comment: Dry N2, 100 mL/min



Sample: I77 # 7
Method: 10°C/min to 1000°C
Comment: Dry N2, 100 mL/min

TGA-DTA

File: C:\ODOT\I77-7.n01
Operator: Supaporn

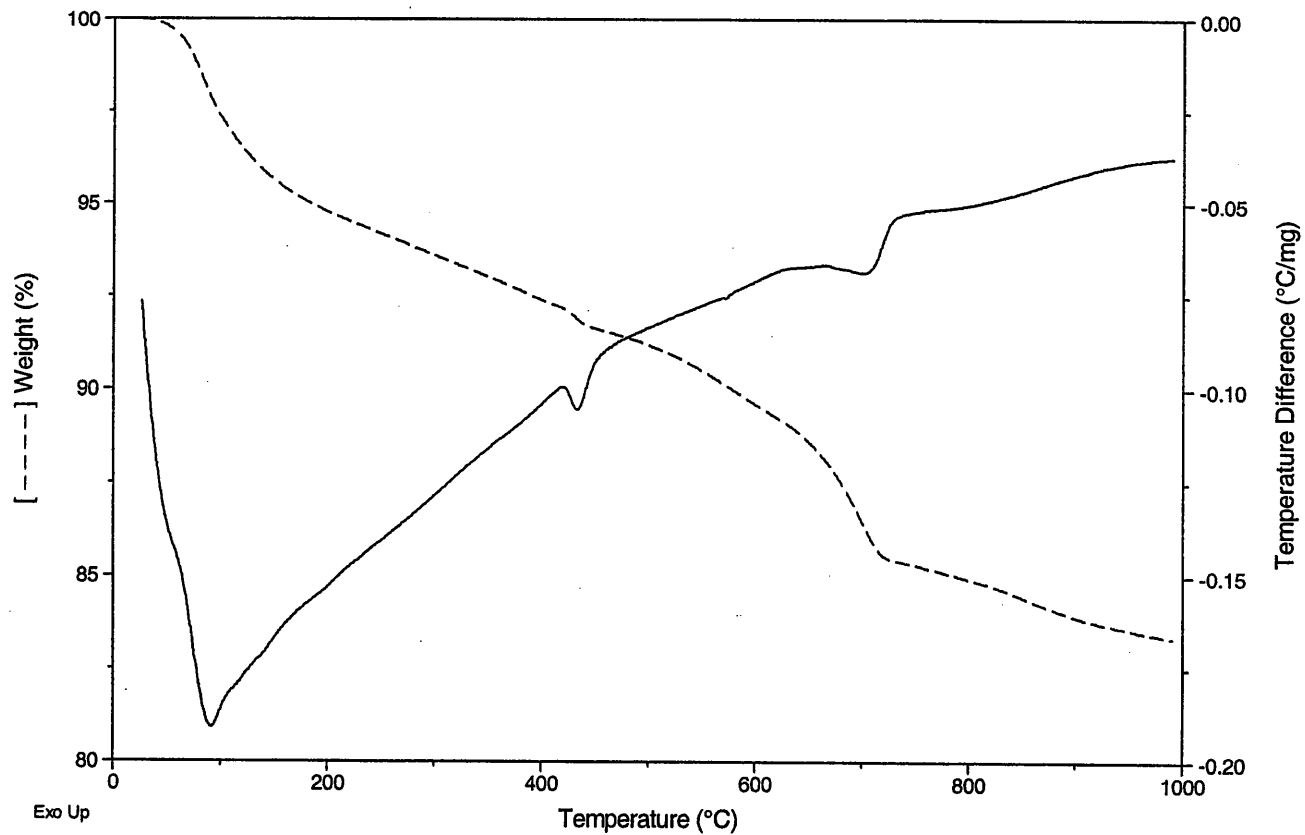


Sample: I77 # 8
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I77-8.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

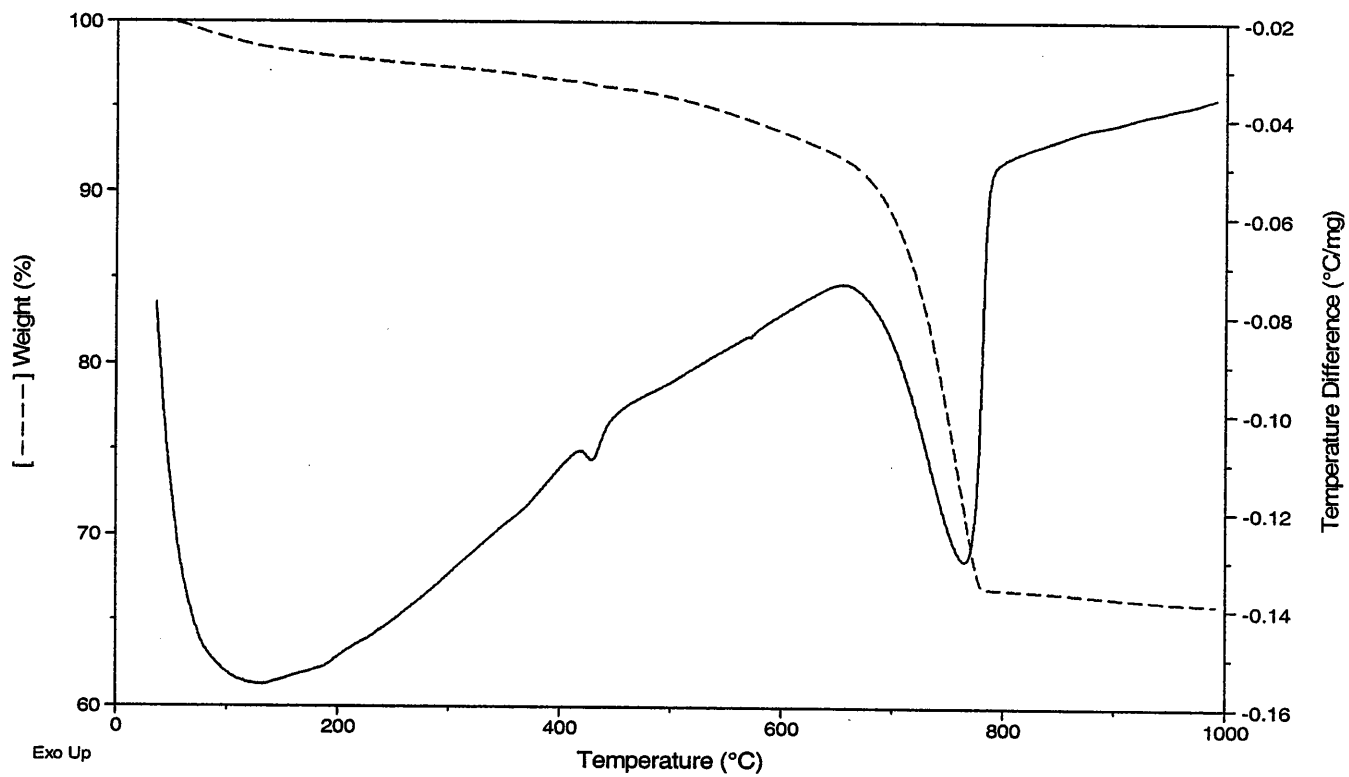


Sample: I90 # 1
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I90-1.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

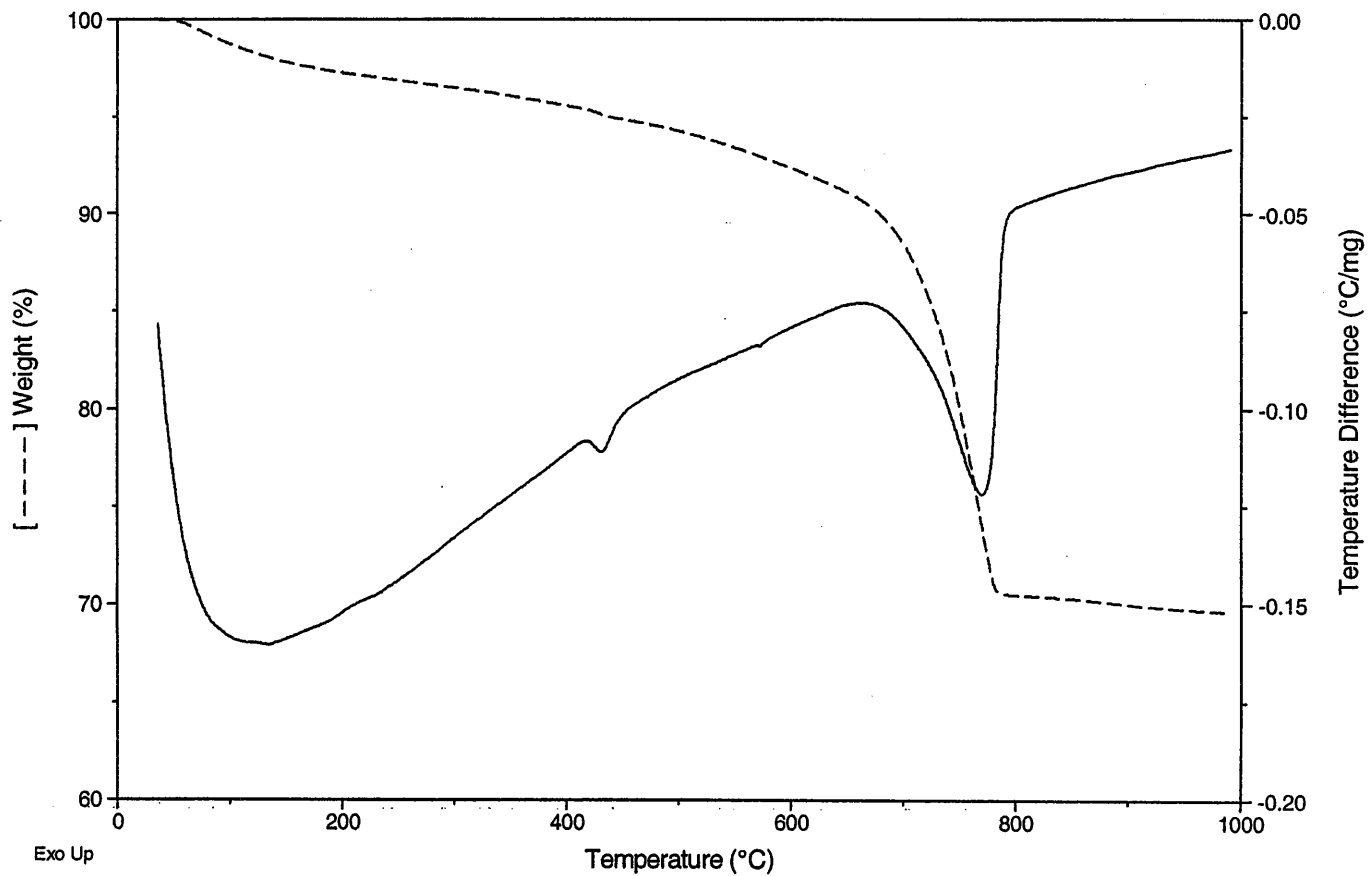


Sample: I90 # 2
Method: 10°C/min to 1000°C

TGA-DTA

File: C:\ODOT\I90-2.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

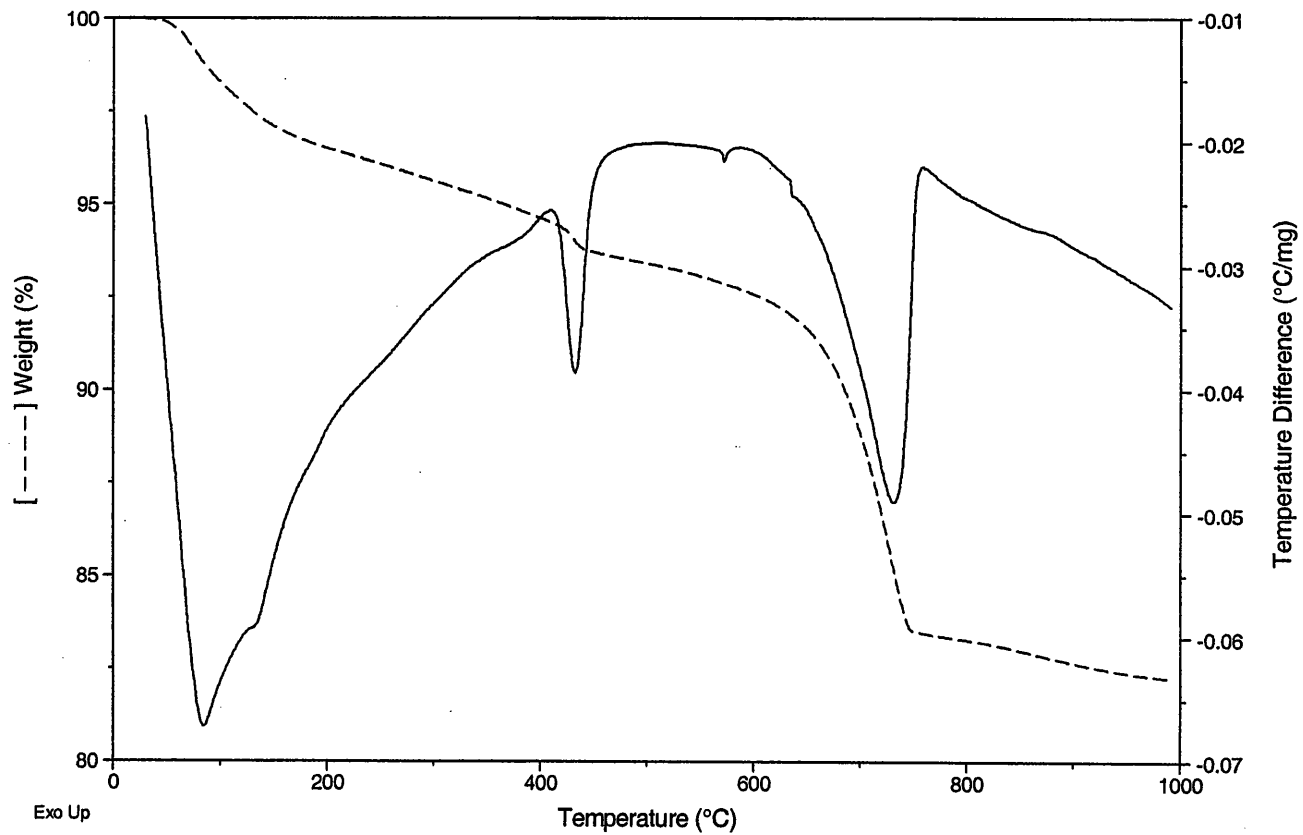


Sample: I90 # 3
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I90-3.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

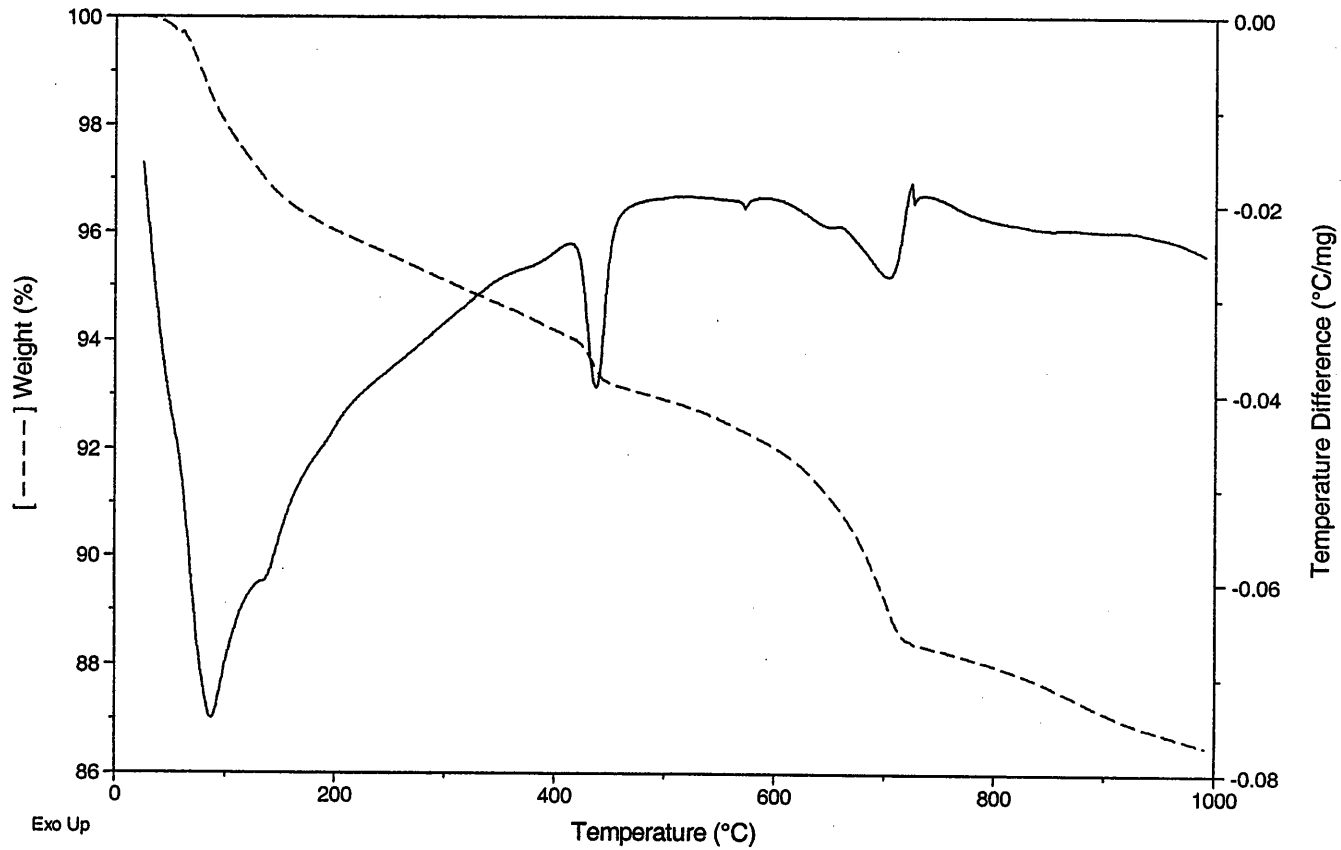


Sample: I90 # 4
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I90-4.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

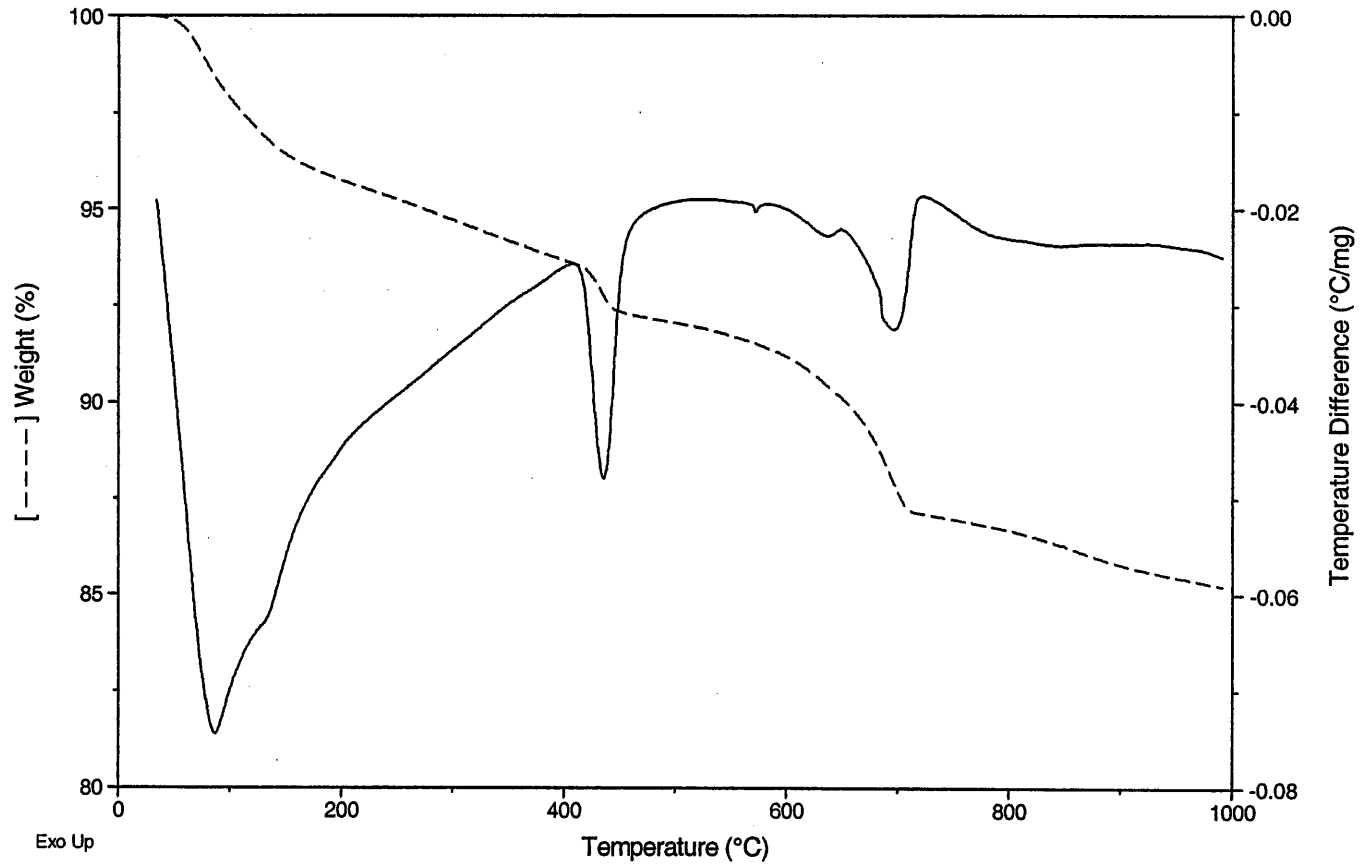


Sample: I90 # 5
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\I90-5.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

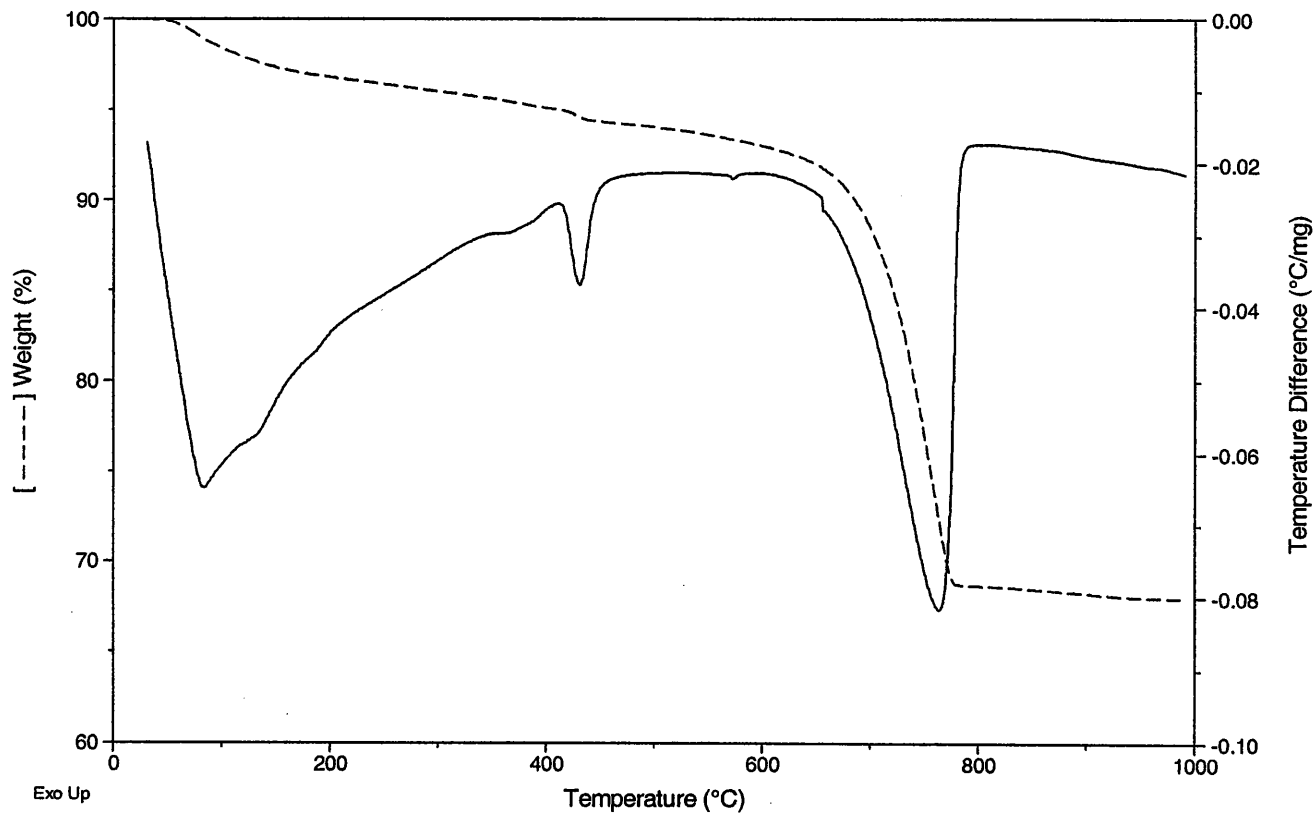


Sample: 190 # 6
Method: 10°C/MIN TO 1000°C

TGA-DTA

File: C:\ODOT\190-6.n01
Operator: Supaporn

Comment: Dry N2, 100 mL/min

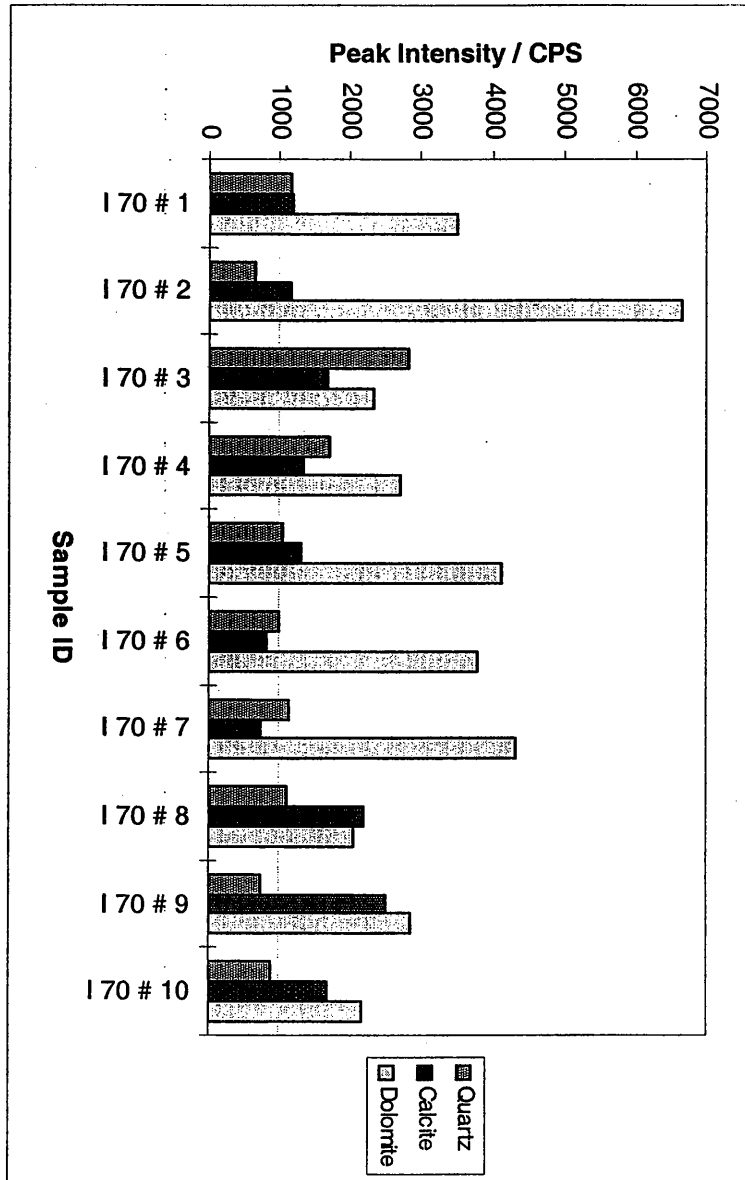


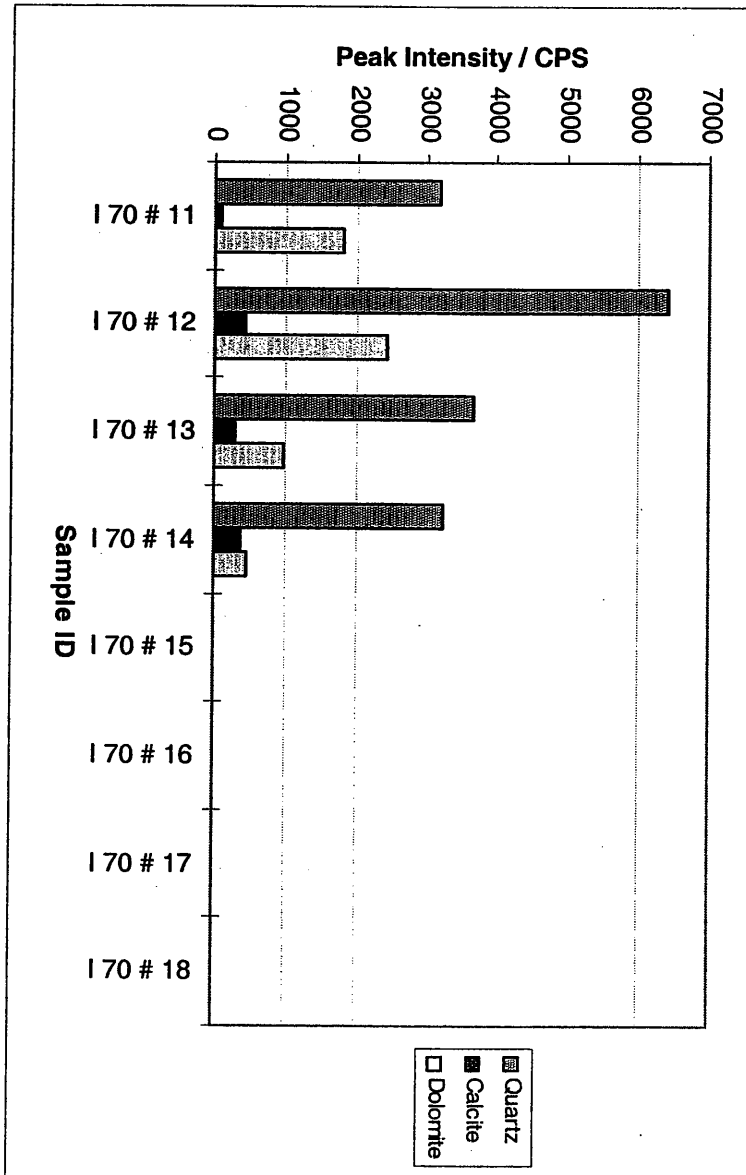
Appendix C

XRD Plots for RPCC Samples from I-70, I-71, I-75, I-77, I-90

Sample ID	Peak Top / CPS		
	Quartz	Calcite	Dolomite
I 70 # 1	1179.3	1205.7	3494.3
I 70 # 2	654.6	1166.9	6660.5
I 70 # 3	2816.3	1672.7	2337.4
I 70 # 4	1712.1	1333.1	2713.0
I 70 # 5	1066.5	1306.9	4117.4
I 70 # 6	985.3	825.9	3794.9
I 70 # 7	1137.4	748.0	4331.7
I 70 # 8	1122.9	2204.9	2061.8
I 70 # 9	735.9	2492.4	2840.5
I 70 # 10	881.5	1675.1	2162.4
I 70 # 11	3171.4	97.4	1817.2
I 70 # 12	6436.9	422.4	2443.2
I 70 # 13	3670.3	300.8	986.9
I 70 # 14	3243.7	368.9	446.5
I 70 # 15			
I 70 # 16			
I 70 # 17			
I 70 # 18			

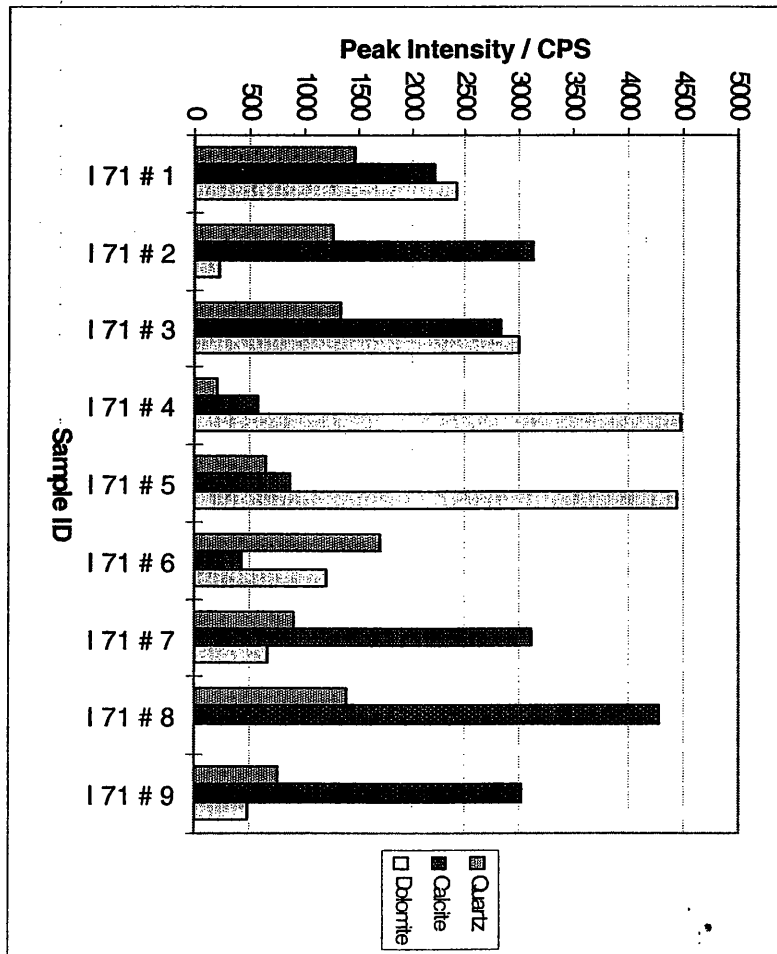
X-Ray Diffraction Observations in Cycles Per Second for All the RPCC Samples from I-70





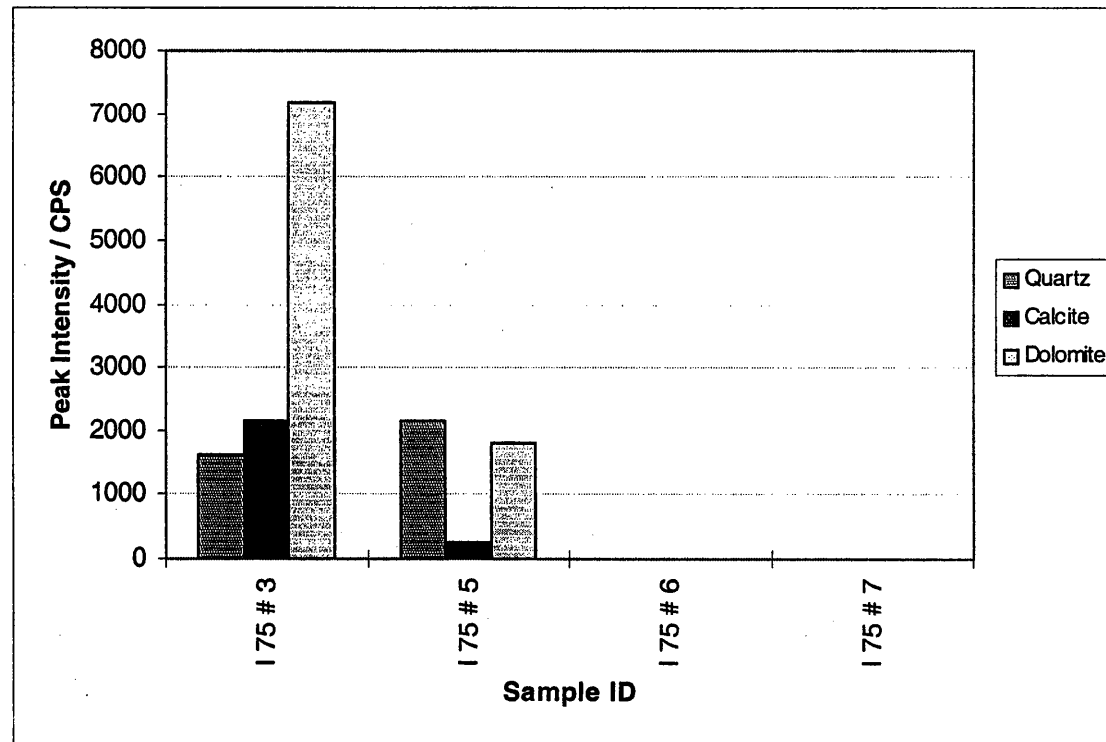
Sample ID	Peak Top / CPS		
	Quartz	Calcite	Dolomite
I 71 # 1	1459.90	2204.20	2422.70
I 71 # 2	1254.90	3117.90	229.50
I 71 # 3	1344.70	2816.20	2984.50
I 71 # 4	208.90	570.30	4475.10
I 71 # 5	650.70	871.90	4449.80
I 71 # 6	1705.30	433.20	1205.40
I 71 # 7	914.20	3099.20	671.70
I 71 # 8	1401.00	4277.30	0.00
I 71 # 9	757.70	3015.10	477.10

X-Ray Diffraction Observations in Cycles Per Second for All the RPCC Samples from I-71



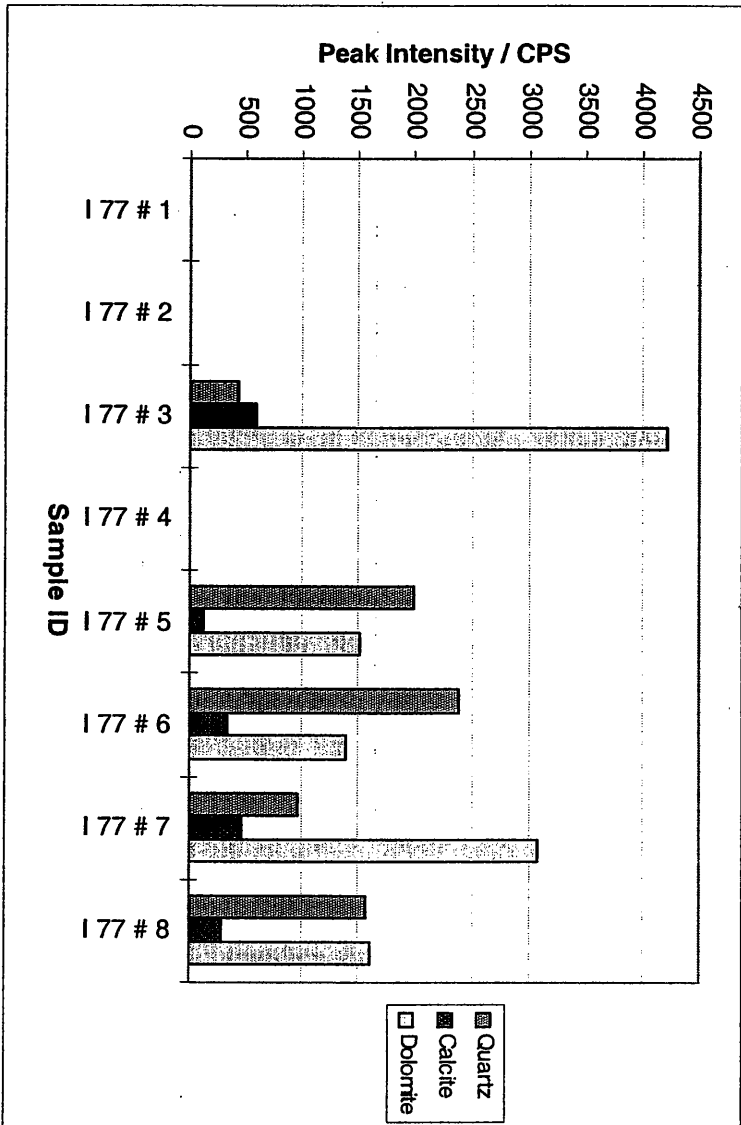
Sample ID	Peak-Top / CPS		
	Quartz	Calcite	Dolomite
I 75 # 3	1605.0	2154.3	7174.0
I 75 # 5	2164.1	265.9	1811.0
I 75 # 6			
I 75 # 7			

X-Ray Diffraction Observations in Cycles Per Second for All the RPCC Samples from I-75



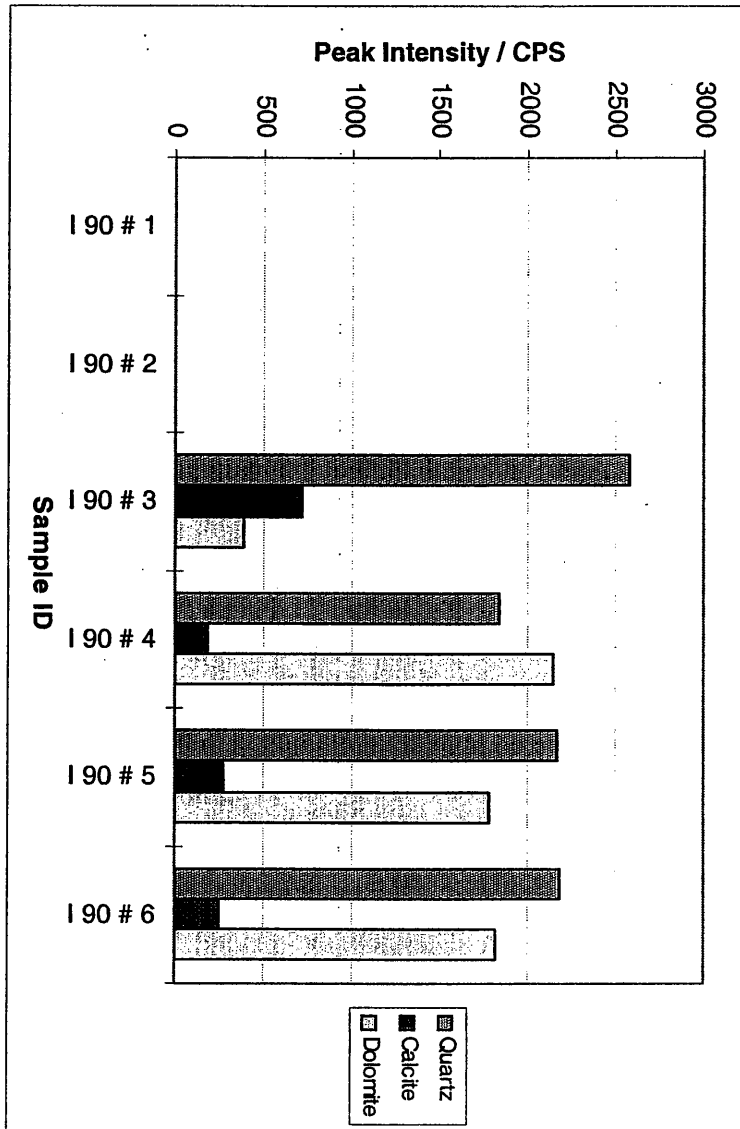
Sample ID	Quartz	Peak Top / CPS	
		Calcite	Dolomite
I 77 # 1			
I 77 # 2			
I 77 # 3	424.0	580.0	4207.3
I 77 # 4			
I 77 # 5	1988.9	130.3	1516.5
I 77 # 6	2381.3	346.2	1385.2
I 77 # 7	964.8	459.8	3068.5
I 77 # 8	1557.0	290.3	1598.3

X-Ray Diffraction Observations in Cycles Per Second for All the RPCC Samples from I-77



Sample ID	Peak Top / CPS		
	Quartz	Calcite	Dolomite
I 90 # 1			
I 90 # 2			
I 90 # 3	2573.3	723.1	391.7
I 90 # 4	1832.8	180.4	2142.7
I 90 # 5	2164.9	274.9	1775.5
I 90 # 6	2173.2	251.8	1808.9

X-Ray Diffraction Observations in Cycles Per Second for All the RPCC Samples from I-90



Appendix D

Operating parameters for Perkin Elmer Plasma II Emission Spectroscopy

Perkin Elmer Plasma II Emission Spectroscopy instrument was used with the following operating parameters to obtain spectroscopy of RPCC samples:

- Power: 1000 watts
- Nebulizer type: cross-flow nebulizer with injection tips molded of Ryton
- Argon flow rate: Auxiliary - 1.0 l/min
Aerosol Carrier - 1.0 l/min
Sampling time - 100 m sec
- Sample aspiration rate: 1.0 mL/min
- Sampling time: 100 msec
- Survey window: 0.100 nm
- Peak window: 0.04 nm
- Observation height: 6 mm above load coil

▪ **ICP-AES Sample Preparation**

Samples were prepared for the ICP – AES experiments using following chemicals:

- 100 ml Calcium Reference Standard, Certified (Fisher Co. Lot # 973626-24) containing CaCO_3 in 2% HNO_3 with the actual concentration of 1005.000 ppm. reported on the certificate of analysis.
- 100 ml Magnesium Reference Standard, Certified (Fisher Co. Lot # 973001-24) containing $\text{Mg}(\text{NO}_3)_2$ in 2% HNO_3 with the actual concentration of 1004.000 ppm reported on the certificate of analysis.
- 500 ml Lanthanum Solution (5% w/w La_2O_3) (Lab Chem. Inc. Lot # 7329-10)
- 2% Nitric Acid (Lab. Prepared)

Appendix E

Procedure to Calculate the Percentage of Free Lime (CaO) in RPCC Samples

Experimental Apparatus

- 50 mL Measuring Cylinder
- 250 mL Erlenmeyer Flask
- 250 mL Vacuum Filtering Flask
- Burette of 0.1 mL Subdivision
- Thermometer (measuring temperature up to 100°C)
- Two-hole Rubber Stopper (Size No. 6) to Fit Erlenmeyer Flask
- Glass Fiber Membrane
- Porcelain Funnel with Rubber to Fit the Vacuum Filtering Flask
- Aluminum Crucibles (to dry the sample in the oven)
- Teflon Coated Magnetic Stirrer Bar
- Hot Plate with Magnetic Stirrer
- Desiccator Filled with Drierite[®]
- Oven
- Vacuum Generator

Chemical

- Anhydrous Ethylene Glycol , Lab Grade, (Lot # 971042, Fisher Scientific Co.)
- 0.05 N HCl (Lot # 7084-6, Lab Chem, actual concentration = 0.0499 N)
- Drierite[®]
- 1 % w/v Phenolphthalein solution (Lab prepared)

Procedure

1. The RPCC samples were ground to a fine powder and then passed through sieve # 275 and retained on # 325.
2. Weigh about 4 g of each sample into an aluminum crucible.
3. Dry the sample in an oven at 110°C for about 1 hr.
4. Let cool in a desiccator.
5. Weigh 1 g of the sample into a clean, dry 250 mL Erlenmeyer flask.
6. Add about 50 mL hot Ethylene Glycol (heated to 70°C). Cover the flask with two-hole rubber (inserted with a thermometer)

1. Heat and stir for 1 1/2 hr. using a magnetic stirrer on a hot plate. The temperature of the solution should be constantly maintained.
2. Set a filtration unit over the 250 mL vacuum filtering flask (wetting the glass fiber membrane with hot ethylene glycol before filtering the solution)
3. Filter the solution through the filtration unit with the aid of vacuum pump.
4. Rinse the Erlenmeyer flask at least twice with about 10 - 15 mL hot ethylene glycol and filtering.
5. Add about 25 mL deionized water into the filtrate (to facilitate the end point determination).
6. Add 3-5 drops Phenolphthalein solution
7. Titrate to colorless end point with 0.05 N HCl

Calculation

$$\% \text{ Free CaO} = \frac{\text{Vol. HCl (mL)} \cdot \text{Normality of HCl} \cdot 28}{10 \cdot \text{Sample Weight (g)}}$$