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1,1,2-TRICHLORO, 1,2,2-TRIFLUOROETHANE (CFC-113) AND WATER ISOTHERM MEASUREMENTS ON IMPREGNATED AND UNIMPREGNATED ACTIVATED CARBONS

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13. ABSTRACT *(Maximum 200 words)*

Impregnated and unimpregnated activated carbon samples were characterized by measuring adsorption equilibria for water and 1,1,2 trichloro, 1,2,2 trifluoroethane (CFC-113). Water adsorption and desorption isotherms were measured at relative humidities (RH) between 20 and 98% at 303 K. The performance of each of these carbons against low boiling toxic vapors at various RH may be estimated using these data. The CFC-113 isotherms were measured at 298 and 348 K over a wide range of vapor phase concentrations from about 10 mg/m^3 to about 5.0×10^4 mg/m^3. The adsorption capacity of several selected carbon samples were compared over the entire concentration range at the two measured temperatures. These data showed that the relative adsorption capacity of two different carbon samples could change depending on the vapor phase concentration. This can be extremely significant if one tries to relate adsorbent performance to surface area measurement (N2 BET) results.

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PREFACE

The work described in this report was authorized under Project No. 10161102A71A, Research in CW/CB Defense. This work was started in January 1991 and completed in September 1991.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

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CONTENTS

LIST OF TABLES

1,1,2-TRICHLORO, 1,2,2-TRIFLUOROETHANE (CFC-113) AND WATER ISOTHERM MEASUREMENTS ON IMPREGNATED AND UNIMPREGNATED ACTIVATED CARBONS

1. INTRODUCTION

Twelve carbon samples were evaluated by measuring water and 1,1,2-trichloro, 1,2,2-trifluoroethane (CFC-113) isotherms. Water isotherms show the available adsorption capacity (total pore volume available) and provide an estimate of the relative adsorption capacities of each carbon in humid environments. The CFC-113 isotherms allow one to estimate the adsorption capacity of each carbon against light reactive vapors over a wide span of challenge concentrations.

Water isotherms were measured using the carbon samples given in Table 1. Both CFC-113 and water isotherms were measured for the carbon samples shown in Table 2.

Table 1. Carbon Samples for Water Isotherm Measurement

Impregnated Activated Carbons	Unimpregnated Activated Carbons
NRADS* 171, Aged 4 weeks	NACAR** TG 214
NRADS 171, Unaged	BPL (Control 3)
Symbiotech 1, H2 + Ethylene	BPL Lot 7BIG-V
Symbiotech 2, HCl + Ethanol	
Diazomethane (Treated BPL Control 3)	
ASC Whetlerite (Lot 1713) (Standard)	

*New reactive adsorbents
**North American Carbon Company

Table 2. Carbon Samples for CFC-113 and Water Isotherm Measurement

ASC Whetlerite Lot #
1765
1761
1776
1792
1713 (Standard)
Superactivated Carbon (MAXSORB)

2. EXPERIMENTATION

2.1 Water Isotherms.

2.1.1 Apparatus.

The details of the equipment used to measure water isotherms are given below in Table 3. Figure A-1 shows the configuration of the water isotherm system.

Table 3. Equipment for Water Isotherm Apparatus

Item	Manufacturer	Model #
Humidity Control System	Miller Nelson Inc.	HCS-301
Dew All Digital Humidity Analyzer	EG&G Inc.	911
Large Mechanical Convection Oven	Precision Scientific	23
Hybrid Chart Recorder	Yokogawa Electric Works	3088
Temperature Controller	Fenwall Inc.	550
Temperature Controller	Omega Engineering	CN300
Variable Autotransformer	Staco Engineering	3PN1010
Fiber Glass Cylinder	Experimental Fab Shop	
Valves, and a Vacuum Source		

The Miller Nelson humidity control system produces the conditioned air stream, which flows at 26.7 standard liters per minute (slpm) through 3/8 in. copper tubing wrapped in heat tape to keep the air temperature close to 303 K. The conditioned air stream enters the large convection oven, which maintains the environment at 303 K. A fiberglass cylinder holds up to 15 carbon samples, the temperature probe from the EG&G Dew All Humidity Analyzer, and tubing from the EG&G Dew Point Hygrometer. Valves connected to a vacuum source are adjusted to pull 1.5 slpm of conditioned air over the carbon samples and EG&G Dew Point Hygrometer.

2.1.2 Procedure.

2.1.2.1 Preparation.

Glass tubes 3-4 in. long and 1/4 in. in diameter held the carbon sample. A mesh screen secured at one end of the tube held the carbon in place. Glass wool plugs at each end helped secure the carbon inside the tube, making sure that no carbon was lost through the vacuum lines. Carbon was inserted into tared empty glass tubes with glass wool plugs, weighed, and dried overnight in a convection oven at 398 K to remove all water adsorbed during the transfer process. After cooling, these tubes were weighed to determine a dry carbon mass.

2.1.2.2 Experiment.

Water isotherm experiments were conducted at 303 K. The relative humidities (RH) used in each experiment were 23, 31, 36, 41.5, 46, 51, 56.5, 61, 65.5, 70, 73.5, 80, 85.5, 90, and 96 (near saturation) for the adsorption portion of the experiment and 88, 83.5, 77.5, 72, 67, 62, 58, 54, 48, 42, 36, 31, and 23 for the desorption portion. The sample tubes were removed and weighed after an equilibration time of approximately 4 hr. Then the RH was adjusted to the next desired value, and the sample tubes were put back into the cylinder for equilibration. All temperatures, RH readings (EG&G and Miller Nelson), and the Dew Point were recorded on the YEW Chart Recorder. During weekends, the samples were stored in a beaker covered with Parafilm.

2.2 CFC-113 Isotherms.

2.2.1 Apparatus.

Figure B-1 shows a schematic of the CFC-113 apparatus. Table 4 lists the equipment used in this experiment.

Table 4. Equipment for CFC-113 Isotherm Apparatus

Item	Manufacturer	Model #
Gas Chromatograph	Hewlett Packard	5880A
Hybrid Chart Recorder	Yokogawa Electric Works	4088
Mass Flow Controller	Tylan	FC262
Pressure Transducer	Validyne	AP10-42
Balance	A&D Co. Limited	FR200, 50031
Constant Temperature Water Bath	Brinkman Instruments	Lauda RM6
Circulating Pump 60HZ	Metal Bellows	MB-41
Auto Inject Valve	Valco Valve, Inc.	VICI
Infrared Spectrometer (IR)	Wilks	MIRAN 80
HPLC Pump	Waters Associates	M-6000A
Variable Autotransformer	Staco Engineering	3PN1010
Temperature Controller	Omega Engineering	CN5001TI

Material is introduced into the closed loop system using a Valco valve and 10 µL injection loop. A high-performance liquid chromatography pump provides a constant flow through the auto injector loop to keep the loop filled. The Tylan mass flow meter measures the circulation rate of air through the closed loop system. The infrared (IR) spectrometer helps determine the equilibration time of CFC-113 in the closed loop and gives a mixing volume for the chemical. Two 4-way Whitey valves help direct flows through the system. The valve configuration shown in Figure B-1 is the closed-loop bypass mode. By changing the bottom valve, flow is directed over the carbon adsorbent. If the top valve is changed, external purge air is introduced through the system. The flow-through bed holding the carbon is a stainless steel tube with a 15-µm frit located inside. The frit is used to keep the carbon and carbon dust from flowing through or lodging in other parts of the system. Glass wool is used to keep the carbon in place. The carbon bed and tubing is submerged in a constant temperature bath for temperature control.

2.2.2 Procedure.

2.2.2.1 Preparation.

The Hewlett-Packard Gas Chromatograph (GC) Model 5880 with a flame ionization detector and a chromosil 310 column was used. Table 5 shows the GC parameter values used in the CFC-113 isotherm experiments.

Table 5. Parameter Values for GC

Oven Temp 75 °C	Nitrogen (carrier gas) flow rate 30 Lpm
Air flow rate 425 Lpm	Threshold 0
Hydrogen flow rate 32 Lpm	Detector 1 Temperature 250 °C
Peak Width = 0.16	
Auxillary 1 Temperature 75 °C	

2.2.2.2 Experiment.

The carbon samples submitted for testing were dried in a convection oven at 398 K overnight, then placed in airtight containers to ensure that the carbon remained dry. Carbon samples were weighed and inserted into the 15-µm frit and stainless steel assembly. The entire assembly is inserted into the closed loop system and submerged in the constant temperature bath. Dry air is purged over the carbon bed for 1 hr to eliminate any water adsorbed during the transfer procedure.

A known concentration of Freon 113 was injected into the closed loop system at atmospheric pressure using a circulation rate of about 6 slpm over the carbon sample. The GC samples were taken to ensure equilibration of the carbon sample at each concentration level. The ending concentration was approximately 50,000 mg/m^3. Isotherms were measured at 298 and 348 K.

3. RESULTS

3.1 Water Isotherm Results.

The method used to determine the water loading (gram of water/gram of carbon) at each RH is given below:

Tube and Carbon
- Tube without Carbon
Dry Carbon

Weight of Tube at first %RH
- Tube without Carbon
Weight of Carbon at that %RH

Weight of %RH Carbon
- Original Dry Carbon
Change in Carbon Weight
(Delta Mass)

Delta Mass/Original Dry Carbon = gram/gram loading

Figures A-2 through A-5 show the results for NRADS 171 Unaged, NRADS 171 Aged, Symbiotech 1 and Symbiotech 2 carbons compared to the standard ASC Lot 1713 impregnated carbon. The (NRADS 171 Unaged carbon demonstrated more hydrophobic behavior adsorbed less water on a gram/gram basis) than NRADS 171 Aged 4 weeks and ASC Lot 1713, up to 65% RH. Both NRADS carbons had a higher capacity for water adsorption at the higher RH (80-100%) than ASC Lot 1713.

Figure A-6 compares NACAR TG 214 to BPL Lot 7BIG-V. NACAR and BPL carbons exhibit similar water adsorption behavior up to 55% RH; however, NACAR has a much higher water adsorption above 80% RH.

Figure A-8 illustrates BPL (Control 3) compared to BPL Lot 7BIG-V showing a lower capacity for water adsorption at high RH levels (80-100%).

Figure A-9 illustrates that Symbiotech 1 and 2 samples have similar water isotherms. When compared to ASC Lot 1713, they adsorbed less water on a gram/gram basis up to about 65% RH but had a higher capacity for water adsorption at 80-100% RH.

The available adsorption capacity for each sample is shown in Figure A-7. This is calculated by subtracting the gram/gram loading at 80% RH from the gram/gram loading at 100% RH. This difference (available adsorption capacity) may be used as a comparative measure of protection at 80% RH against volatile gases, assuming chemical reaction rates are the same.

Figure A-10 compares water isotherms for Diazomethane and BPL Control 3. These isotherms are very similar throughout the entire RH range.

Water isotherms for Diazomethane and BPL Lot 7BIG-V given in Figure A-11 show no difference in loading capacity up to

60% RH. The BPL Lot 7BIG-V shows a higher capacity for water adsorption up to 60% RH. The BPL Lot 7BIG-V shows a higher capacity for water adsorption and adsorbs more water on a gram/gram basis (Figure A-7) than the Diazomethane between 60 and 100% RH. Diazomethane and BPL Control 3 displayed similar water isotherms (Figure A-10). This result indicates that the total pore volume, the chemical nature of the surface, and the pore size distribution of these two materials are similar. BPL Control 3 compared to the BPL Lot 7BIG-V (standard) indicates that the BPL Control 3 sample is from a less activated lot than our standard.

3.2 CFC-113 Isotherm Results.

Results are shown in Appendix B. These plots compare each carbon with the standard ASC Whetlerite Lot 1713 used in military filters or BPL Lot 7BIG-V. The plots show the natural log of the concentration versus the gram/gram loading.

Each point is calculated as follows:

Q1 and Q2 represent calibration coefficients

$$mg = Q1 * AREA + Q2 * (AREA)^2$$

concentration = milligram/volume of the system

$$\text{loading} = \frac{\#\ \text{injections} * \text{mg/injection } (\mu L) - \text{mg vapor phase}}{\text{original amount of dry carbon}}$$

Figures B-2 through B-7 compare ASC Whetlerite Lots 1792, 1761, and the standard ASC Whetlerite Lot 1713. ASC Whetlerite Lots 1792 and 1761 demonstrated a higher loading capacity than the standard ASC Whetlerite Lot 1713. Based on these results, a 7% difference in breakthrough times for nonreactive adsorbates can be expected based on the adsorption capacity at a concentration between 50,000 and 60,000 mg/m^3.

Figures B-8 through B-13 compare ASC Whetlerite Lots 1765, 1776, and the standard ASC Whetlerite Lot 1713. ASC Whetlerite Lot 1765 and 1776 demonstrated a similar loading capacity to the standard ASC Whetlerite Lot 1713. No difference in breakthrough times for nonreactive adsorbates should result based on the adsorption capacity measured in these experiments.

Figures B-14 through B-16 illustrate Superactivated Carbon (MAXSORB) and BPL Lot 7BIG-V (standard). MAXSORB showed a lower CFC-113 loading at low concentration levels, but much higher loading when near saturation (high concentration level). Figure B-15 compares MAXSORB and BPL Lot 7BIG-V at 298 K. These results imply that the breakthrough time of CFC-113 on BPL at low concentrations could be much longer than the MAXSORB, while at higher concentrations, the situation could reverse. Surface area measurements performed using a QUANTISORB Nitrogen BET apparatus, indicated the surface area of the MAXSORB to be about 2 times higher than BPL carbon surface area. Therefore, if one based the performance of each adsorbent on surface area measurements, one would assume the MAXSORB carbon to have a longer protection time than the BPL carbon at low concentrations (e.g., 1.0 mg/L). These data show, based on equilibrium considerations, that the BPL carbon has superior capacity for CFC-113 at low concentrations.

4. CONCLUSIONS

The following conclusions are provided as a result of the study conducted:

- When evaluating surface treatment effects on activated carbon, one must always measure base-line data on the specific lot treated.

- Surface area measurements (i.e., total pore capacity) may not reflect adsorption capacities at low challenge concentrations.

- Measured water and CFC-113 isotherms provide useful adsorbent structure and performance information.

APPENDIX A

WATER ISOTHERM SCHEMATIC AND DATA

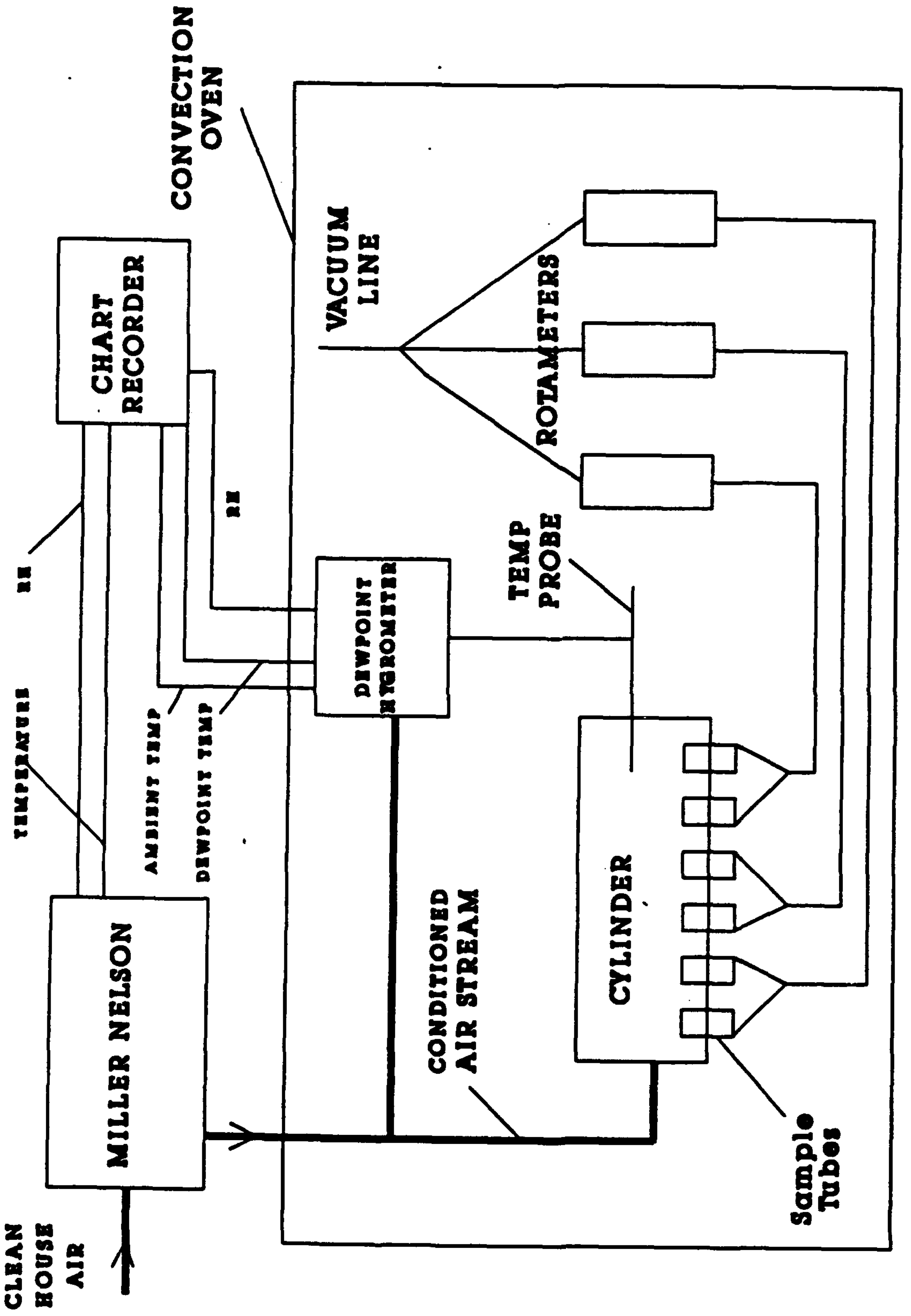

Figure A-1. Water Isotherm Schematic

APPENDIX A

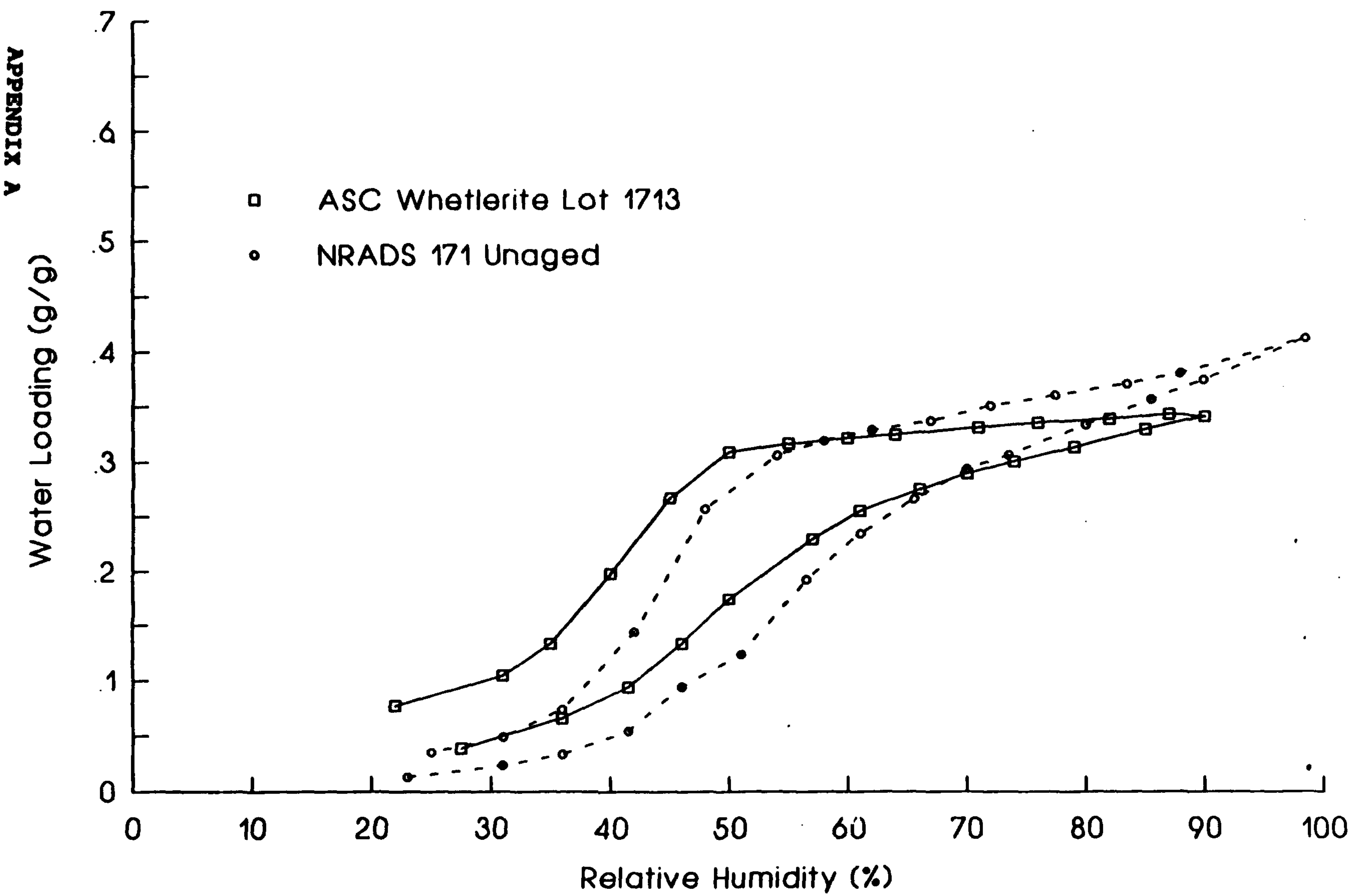

Figure A-2. ASC Whetlerite Lot 1713 and NRADS 171 Unaged

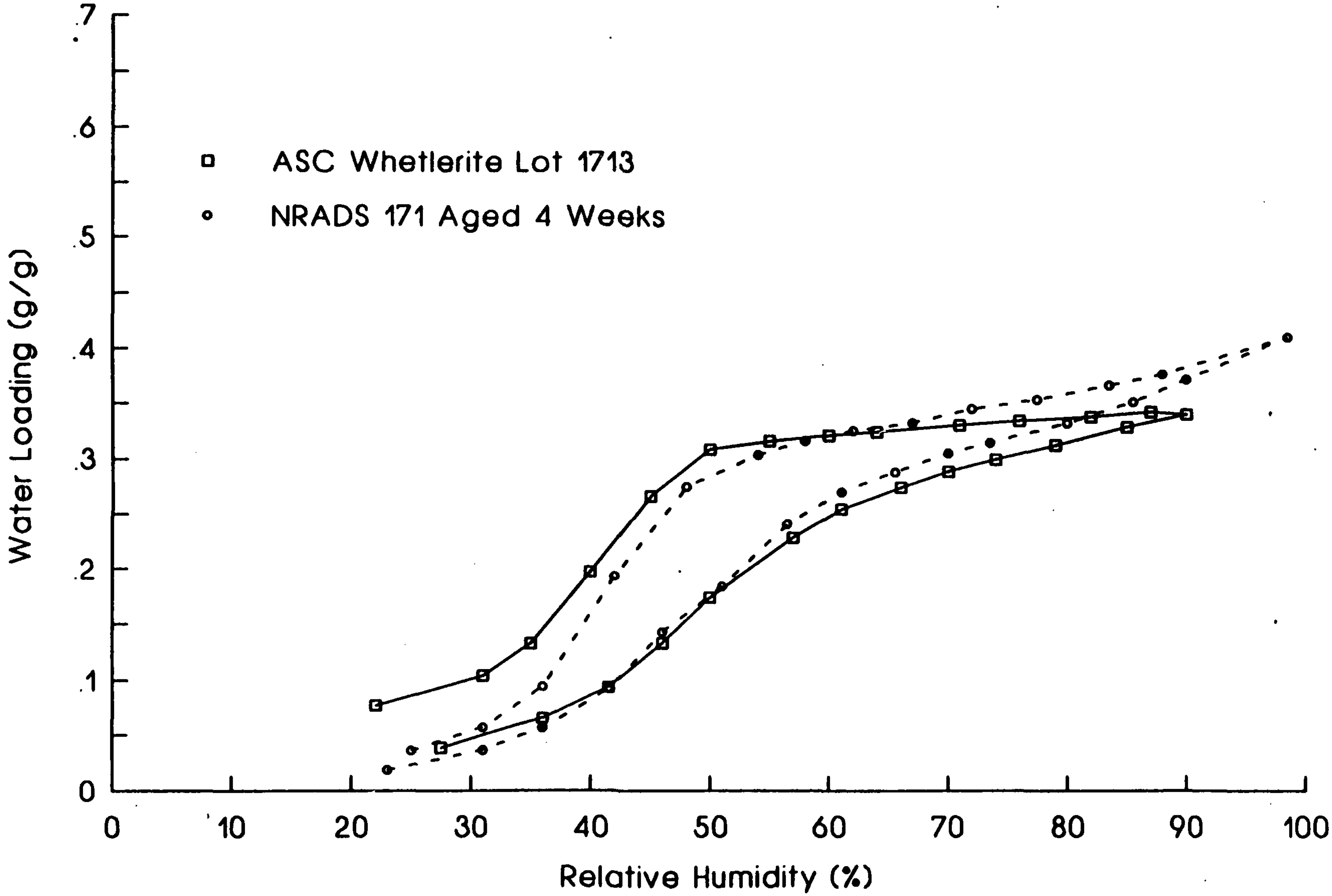

Figure A-3. ASC Whetlerite Lot 1713 and NRADS 171 Aged 4 Weeks

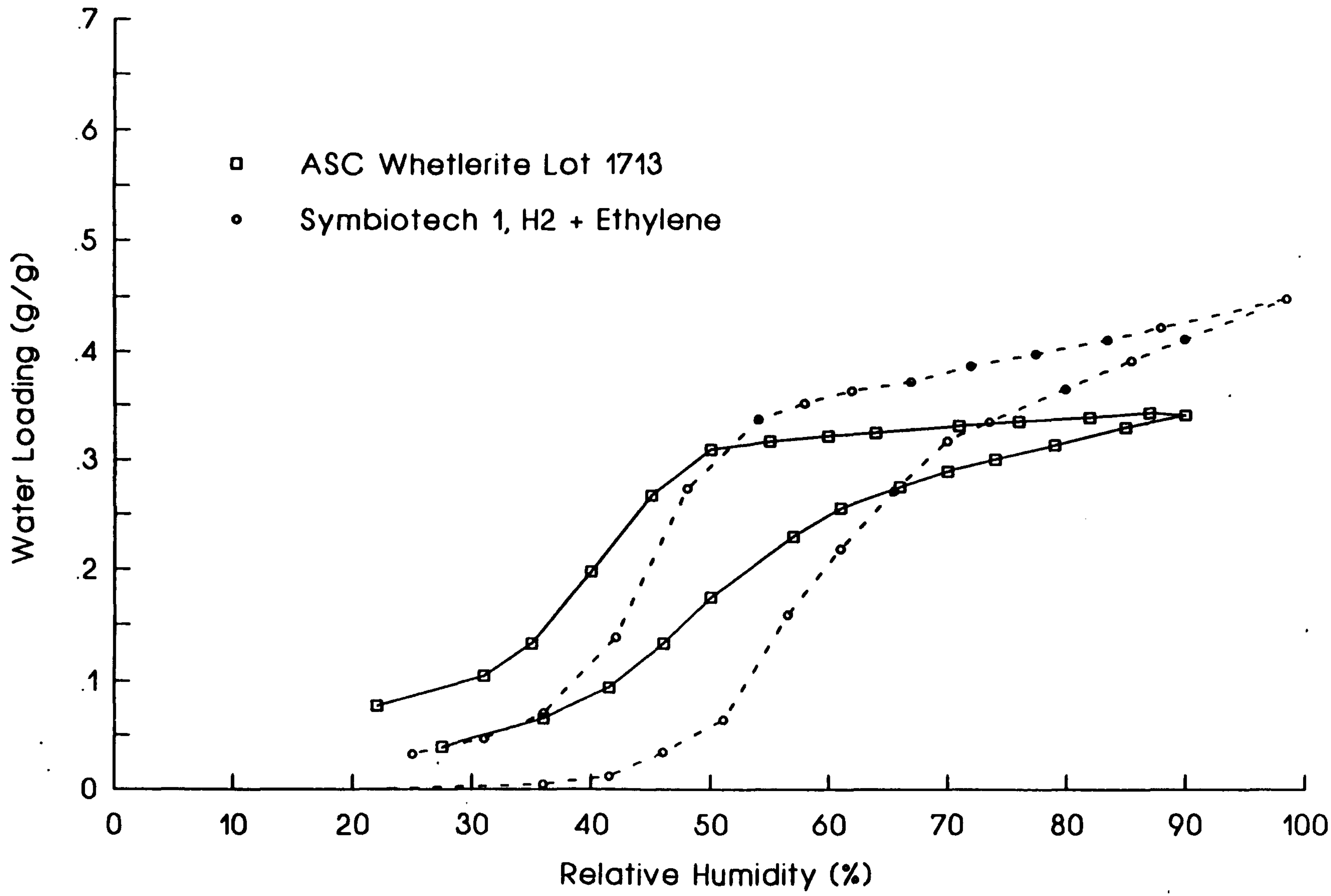

Figure A-4. ASC Whetlerite Lot 1713 and Symbiotech 1

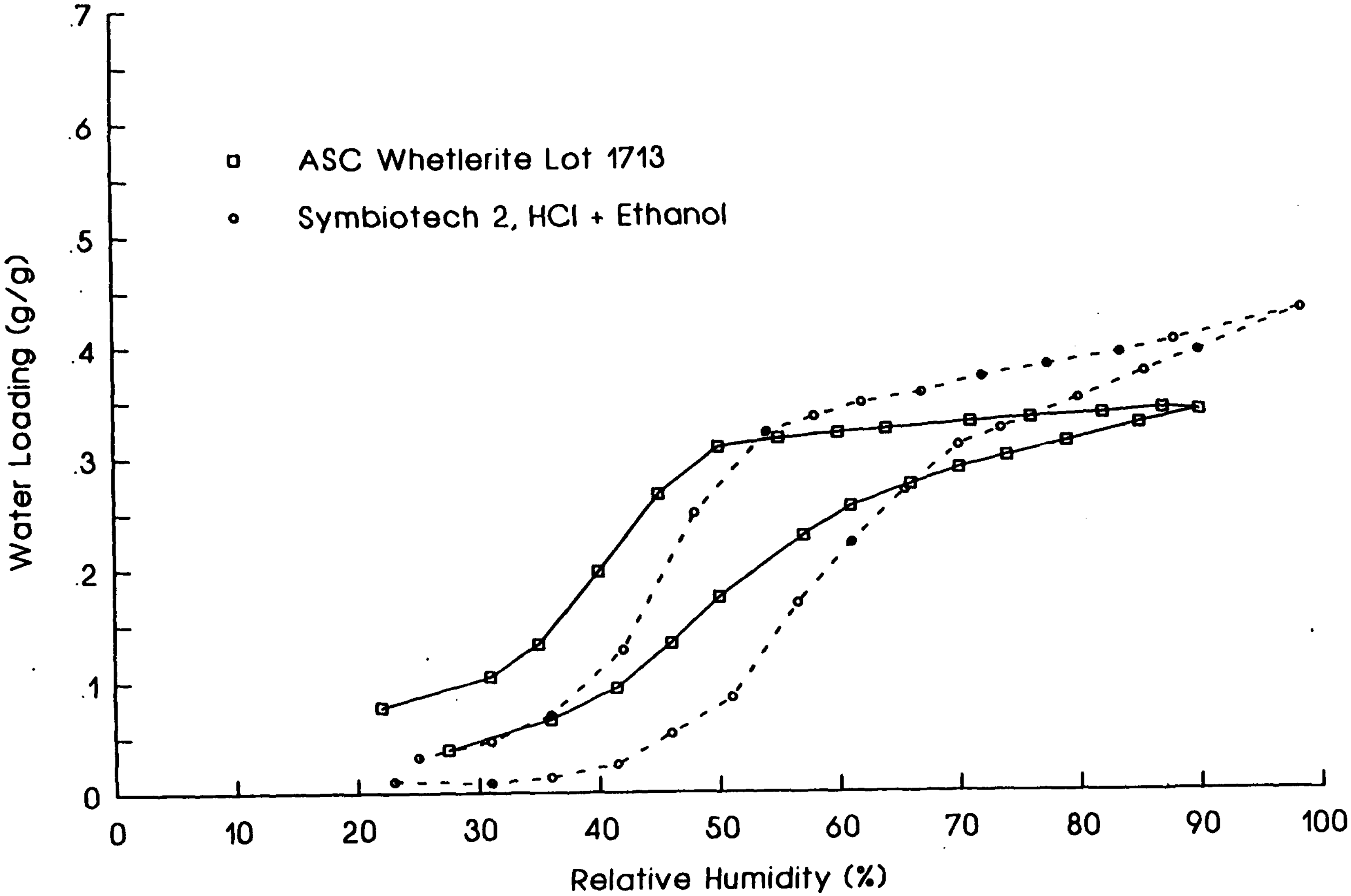

Figure A-5. ASC Whetlerite Lot 1713 and Symbiotech 2

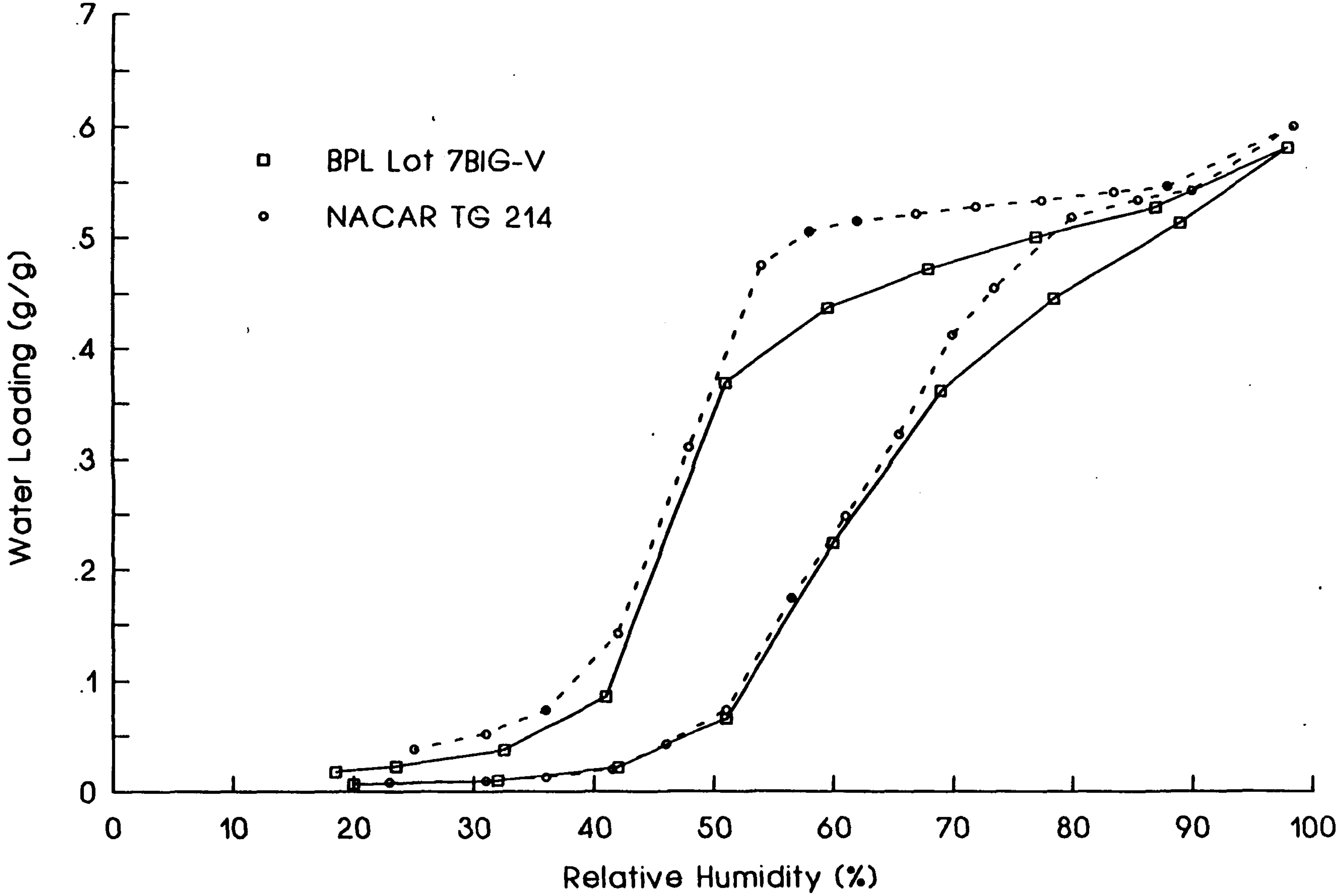

Figure A-6. BPL Lot 7BIG-V and NACAR TG 214

g/g Loading

Carbon Sample	50%RH	80%RH	100%RH
Standard (ASC Lot 1713)	.172	.3124	.3628
Standard (BPL 7BIG-V)	.0648	.4167	.508
NRADS 171 Aged 4 Weeks	.1847	.3331	.4114
NRADS 171 Unaged	.1236	.3336	.4124
NACAR TG 214	.0739	.5182	.6004
BPL (Control 3)	.0704	.3783	.4662
Symbiotech 1, H_2 + Ethylene	.0649	.3652	.4486
Symbiotech2, HCl + Ethanol	.085	.3522	.4326
Diazomethane	.0594	.3773	.4898
MAXSORB	.0138	.5733	.9777

Figure A-7. Comparative Loadings for Water Isotherms

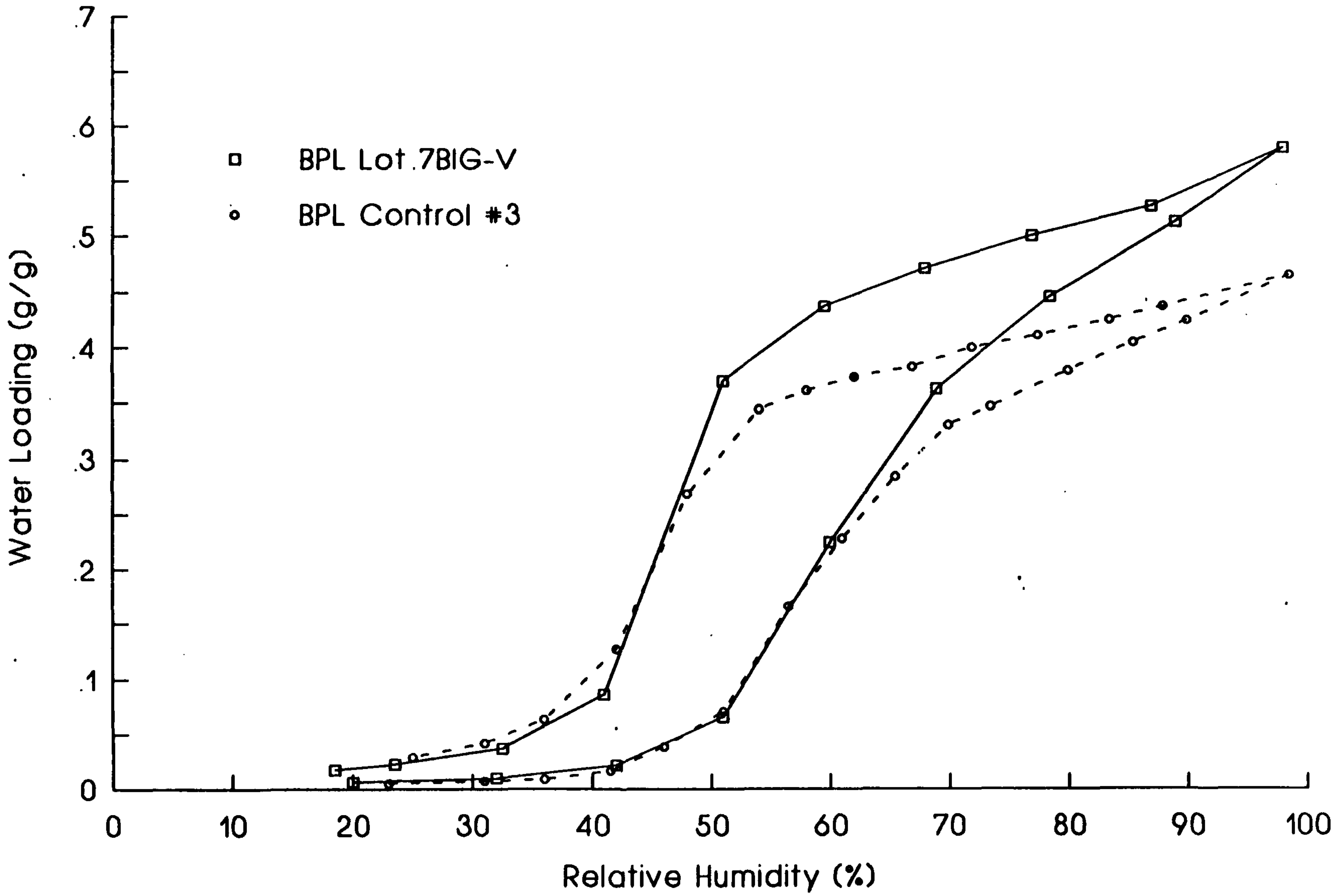

Figure A-8. BPL Lot 7BIG-V and BPL Control #3

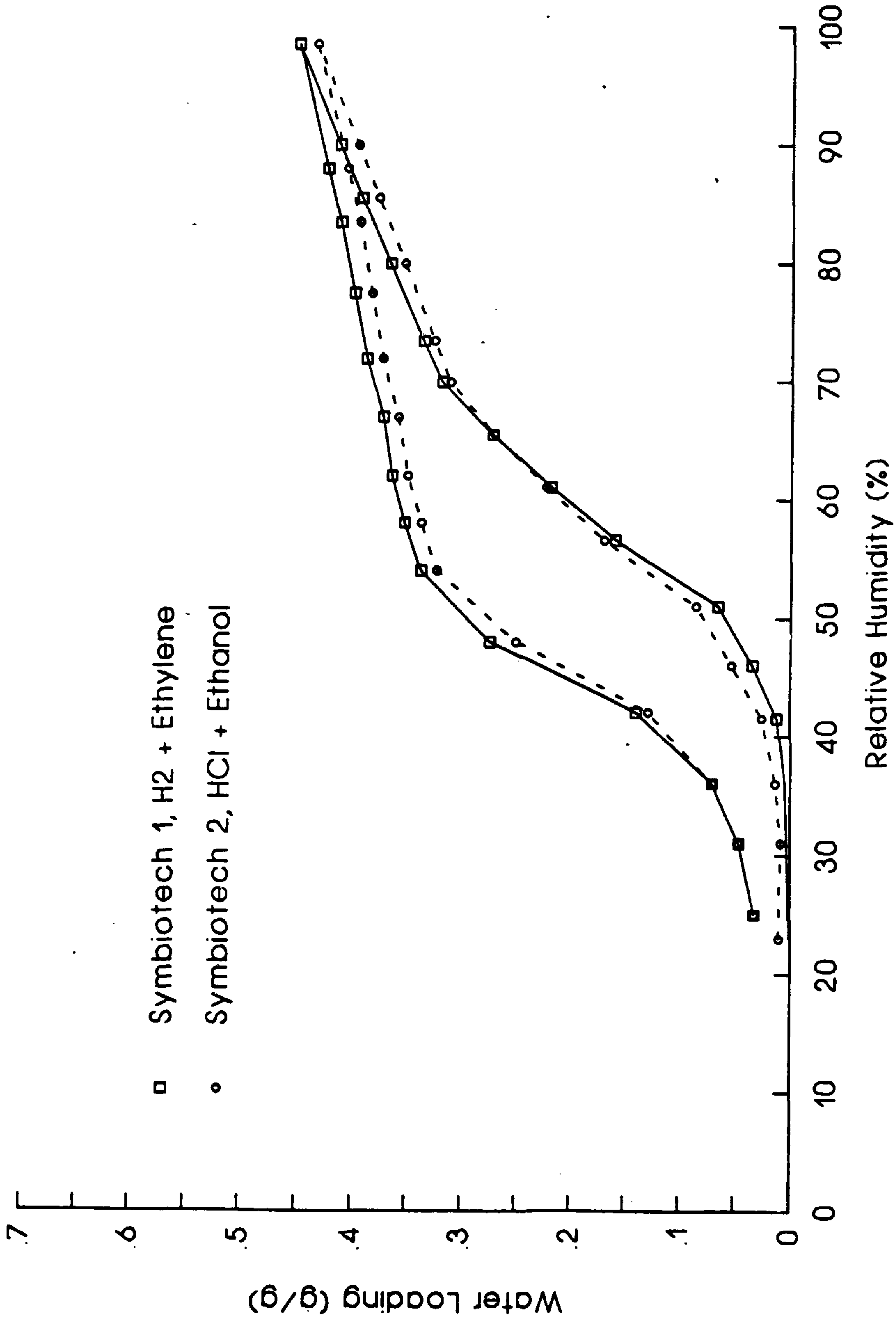

Figure A-9. Symbiotech 1 and Symbiotech 2

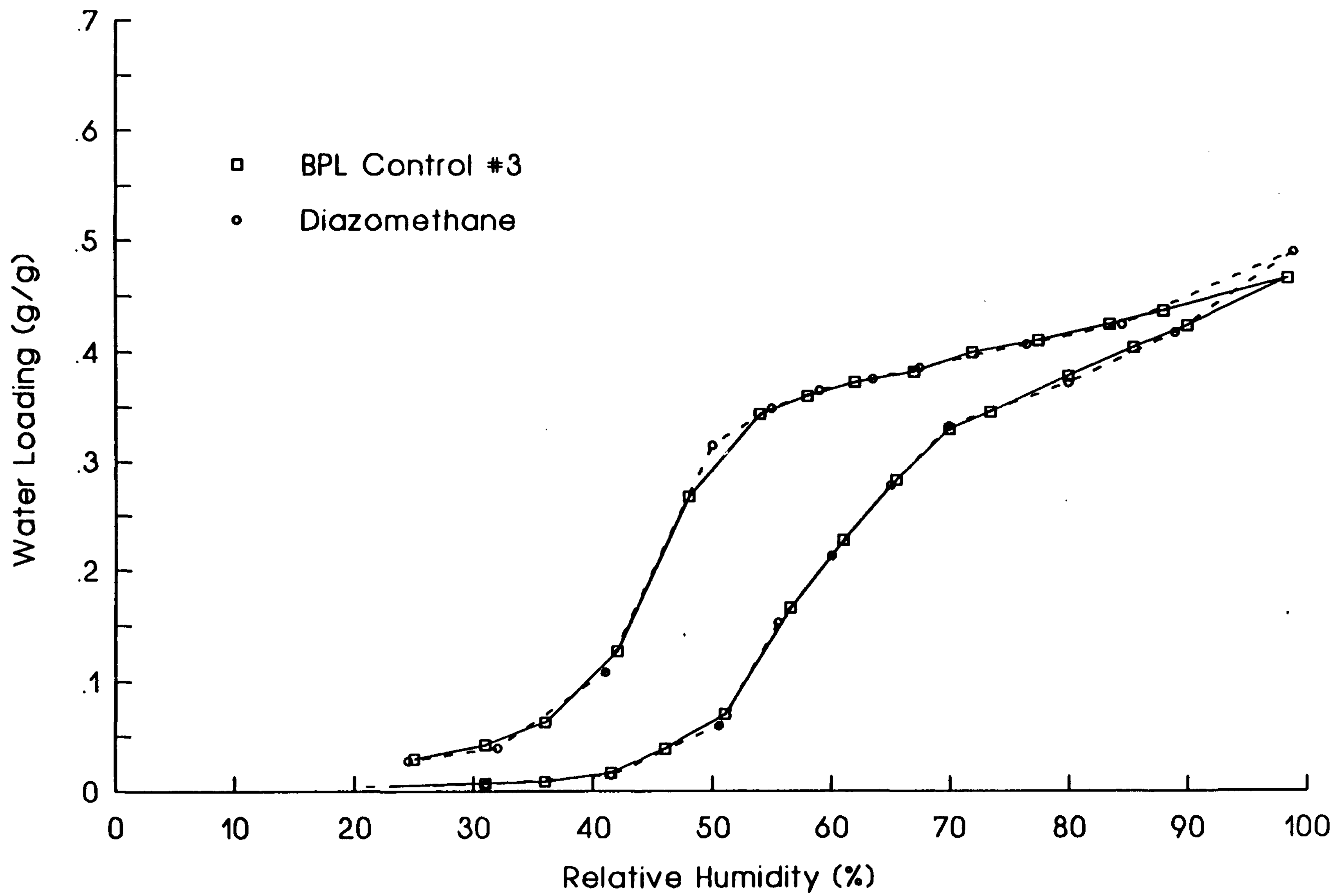

Figure A-10. BPL Control #3 and Diazomethane

APPENDIX A

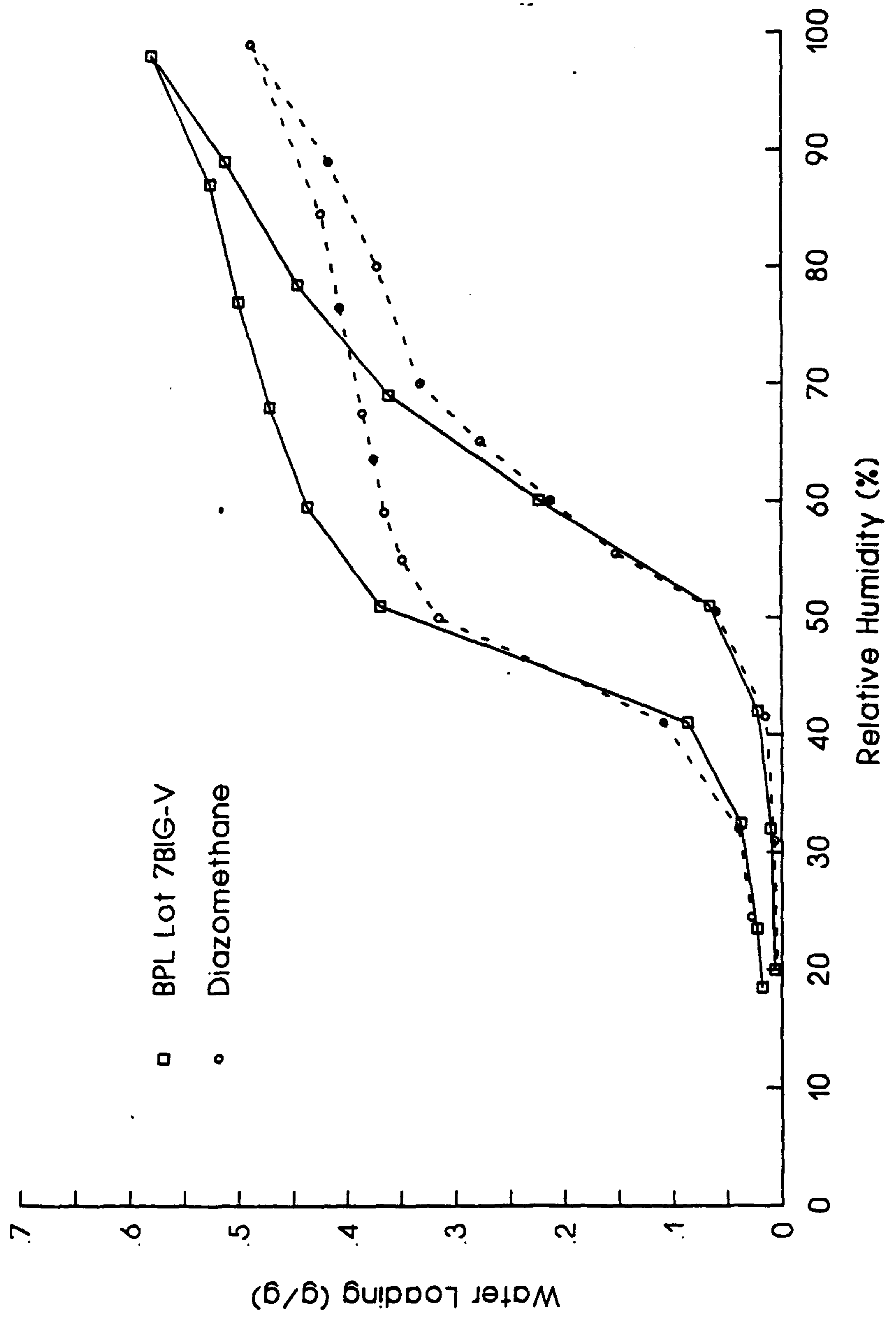

Figure A-11. BPL Lot 7BIG-V and Diazomethane

APPENDIX B

CFC-113 ISOTHERM SCHEMATIC AND DATA

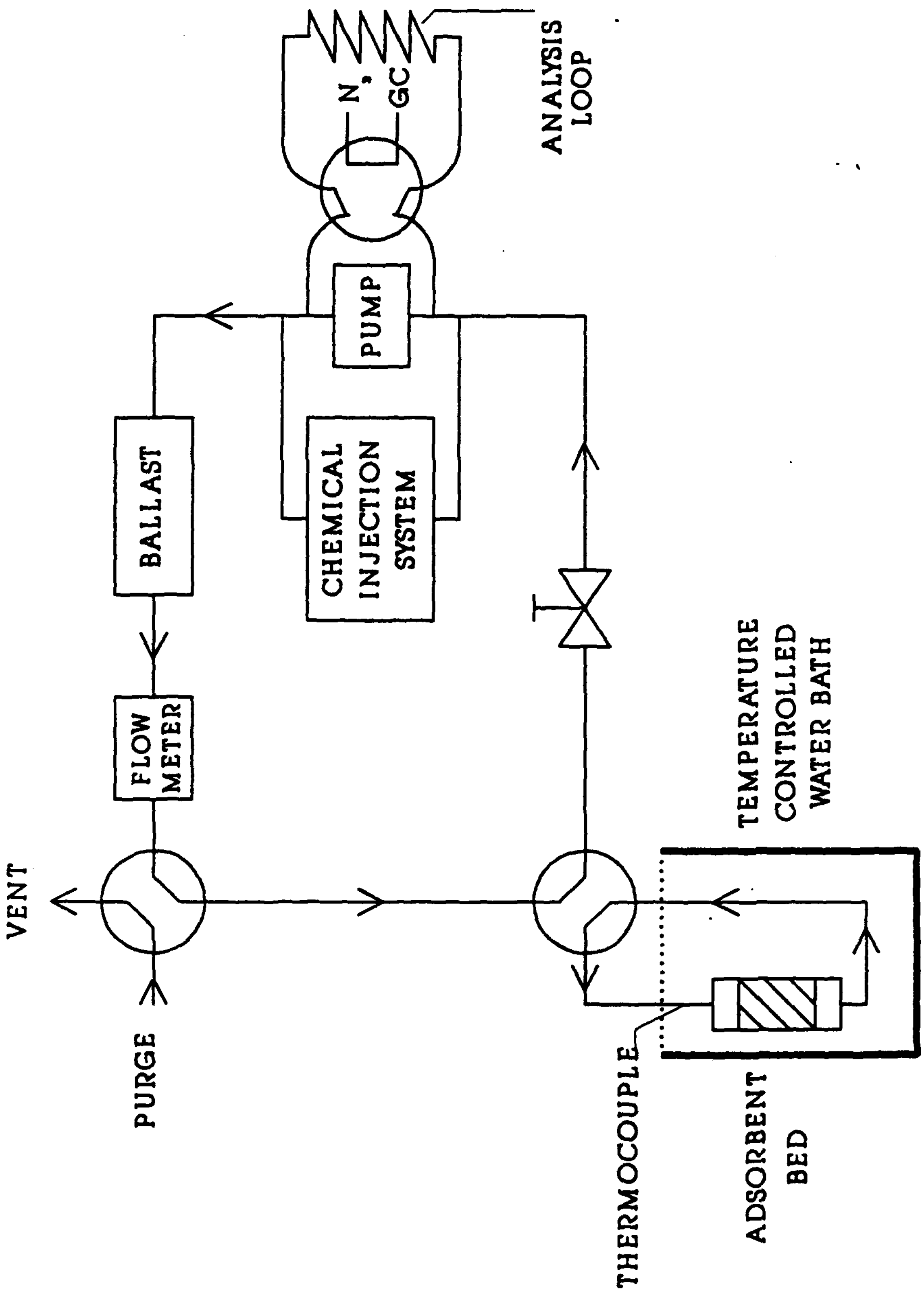

Figure B-1. CFC-113 Isotherm Schematic

APPENDIX B

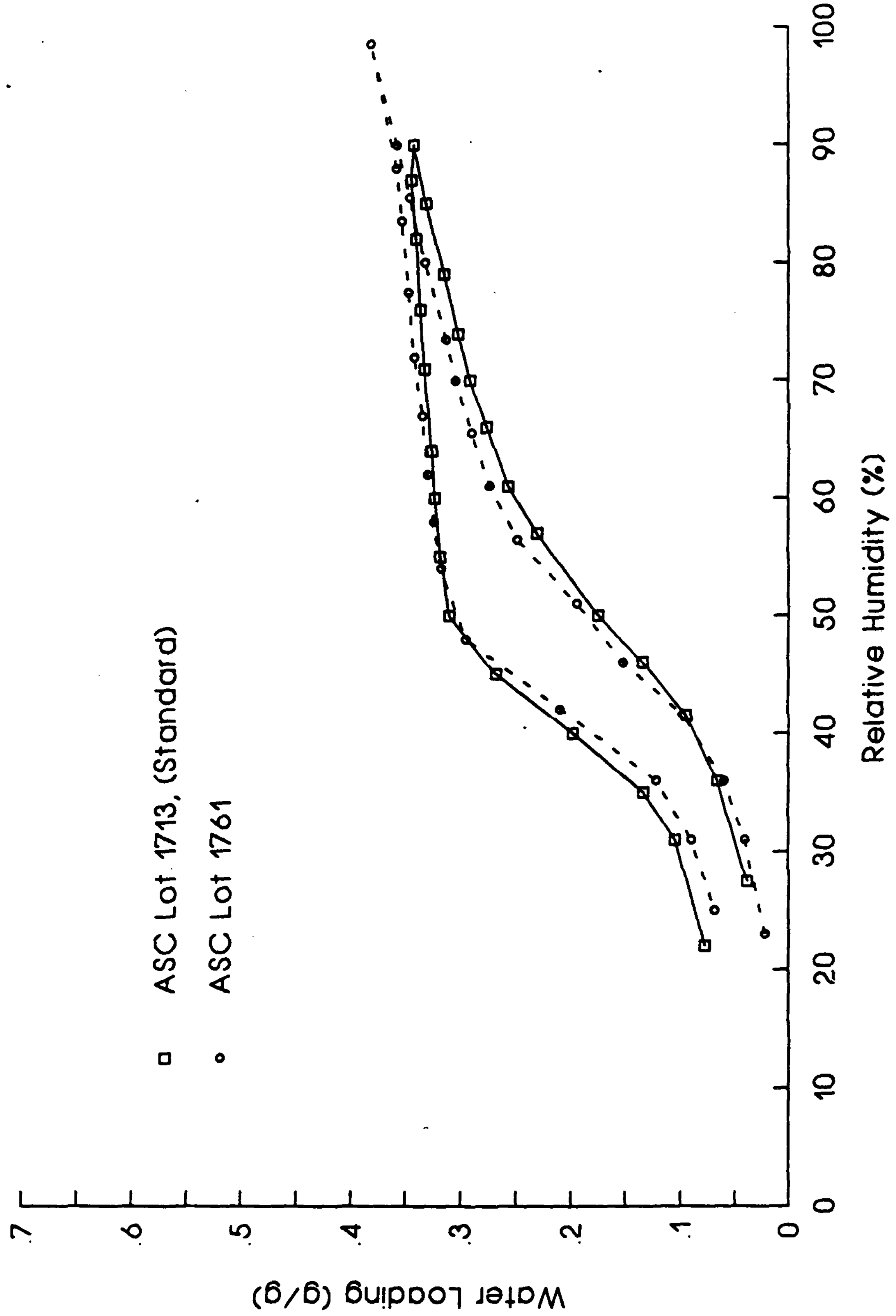

Figure B-2. ASC Whetlerite Lots 1713 and 1761

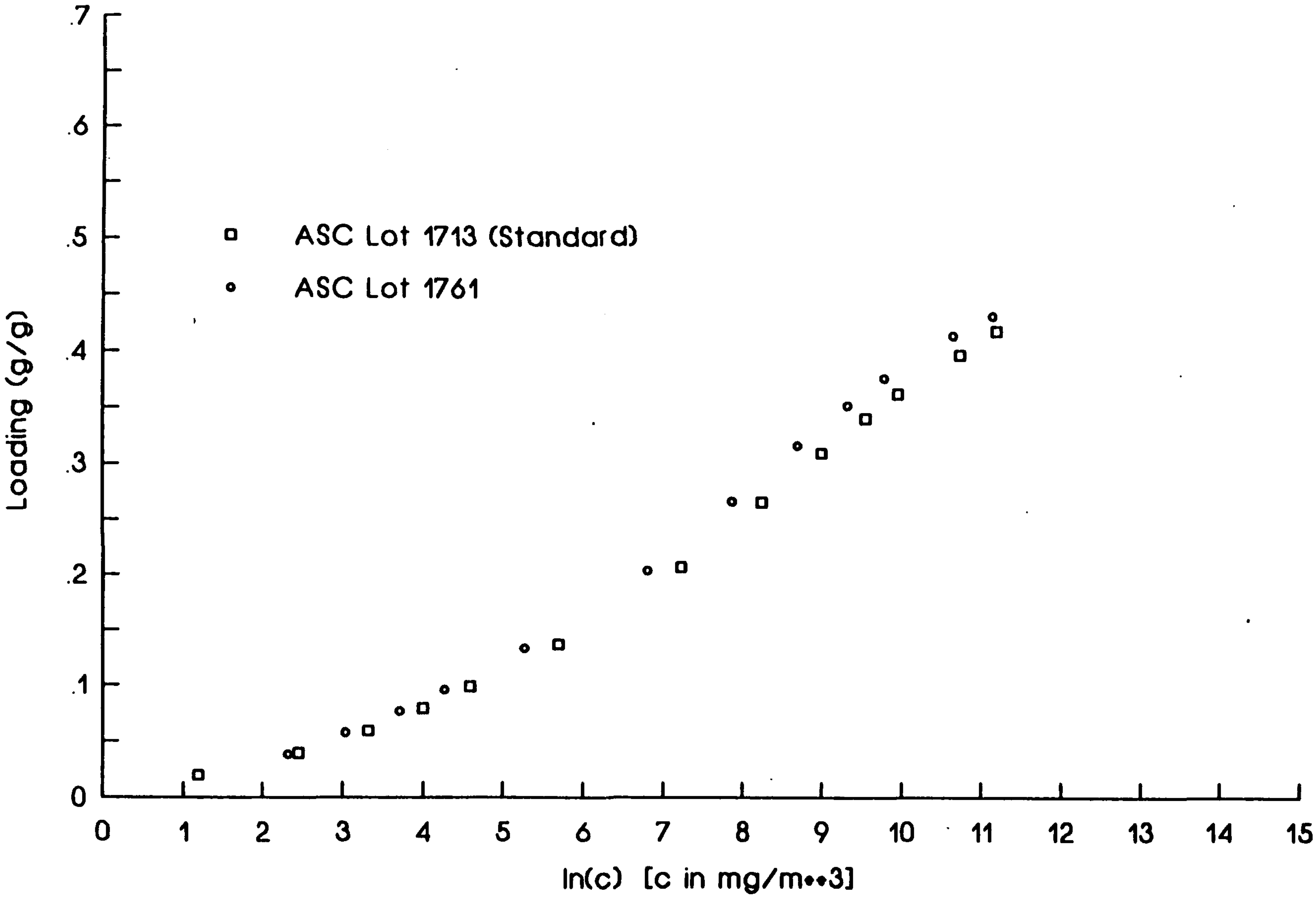

Figure B-3. CFC-113 Isotherms
ASC Whetlerite Lots 1713 and 1761 at 298 K

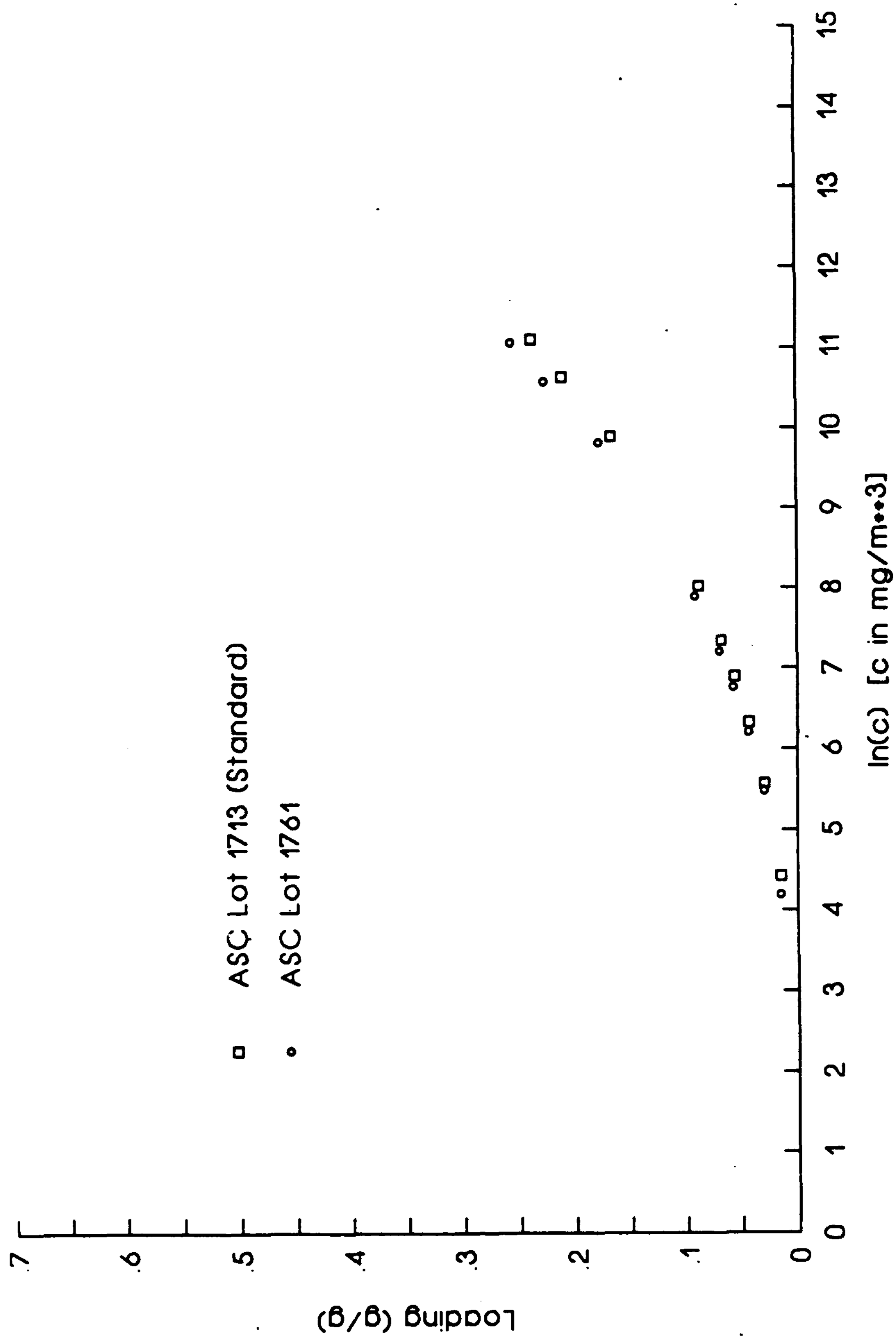

Figure B-4. **CFC-113 Isotherms**
ASC Whetlerite Lots 1713 and 1761 at 348 K

APPENDIX B

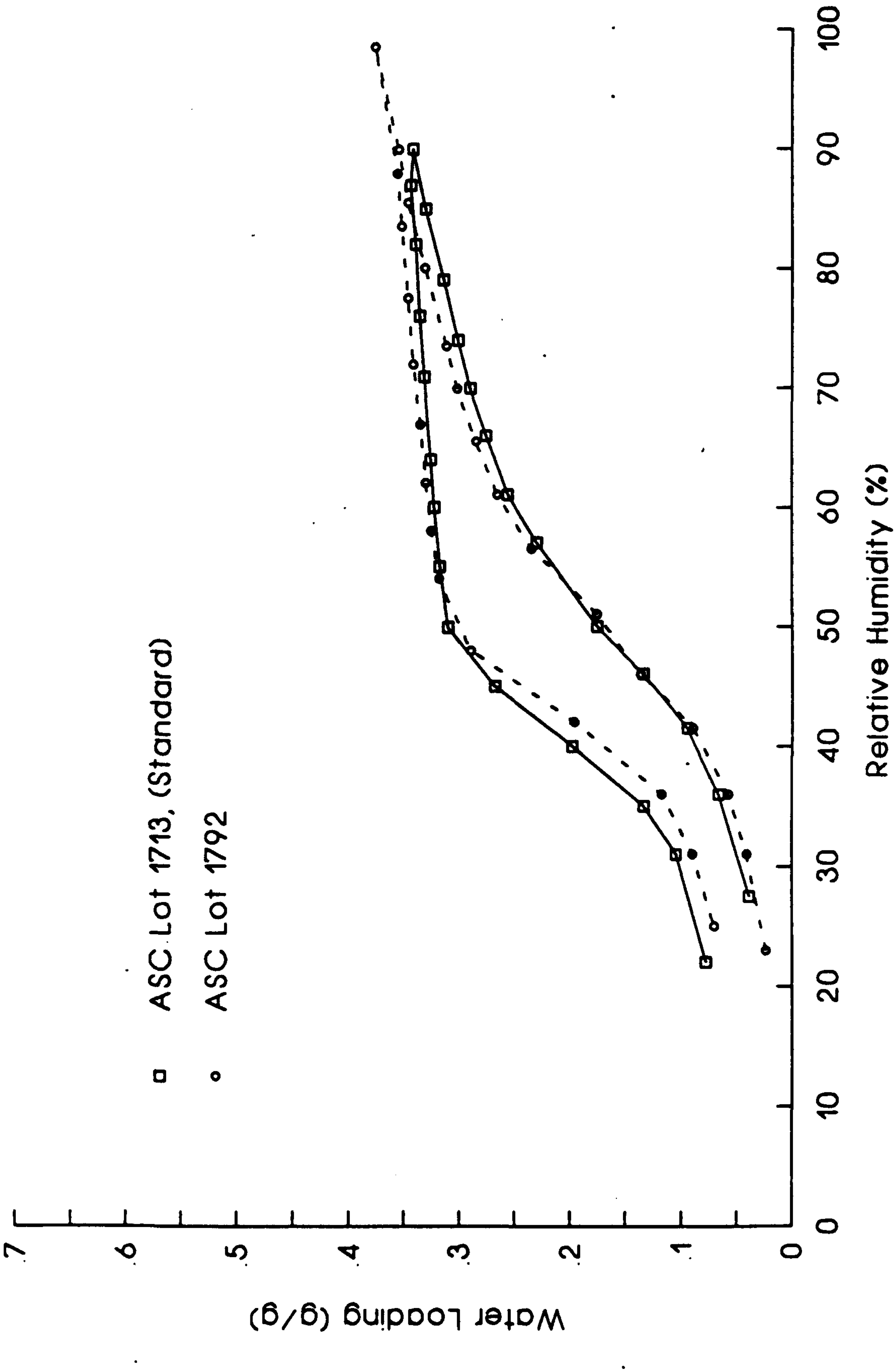

Figure B-5. ASC Whetlerite Lots 1713 and 1792

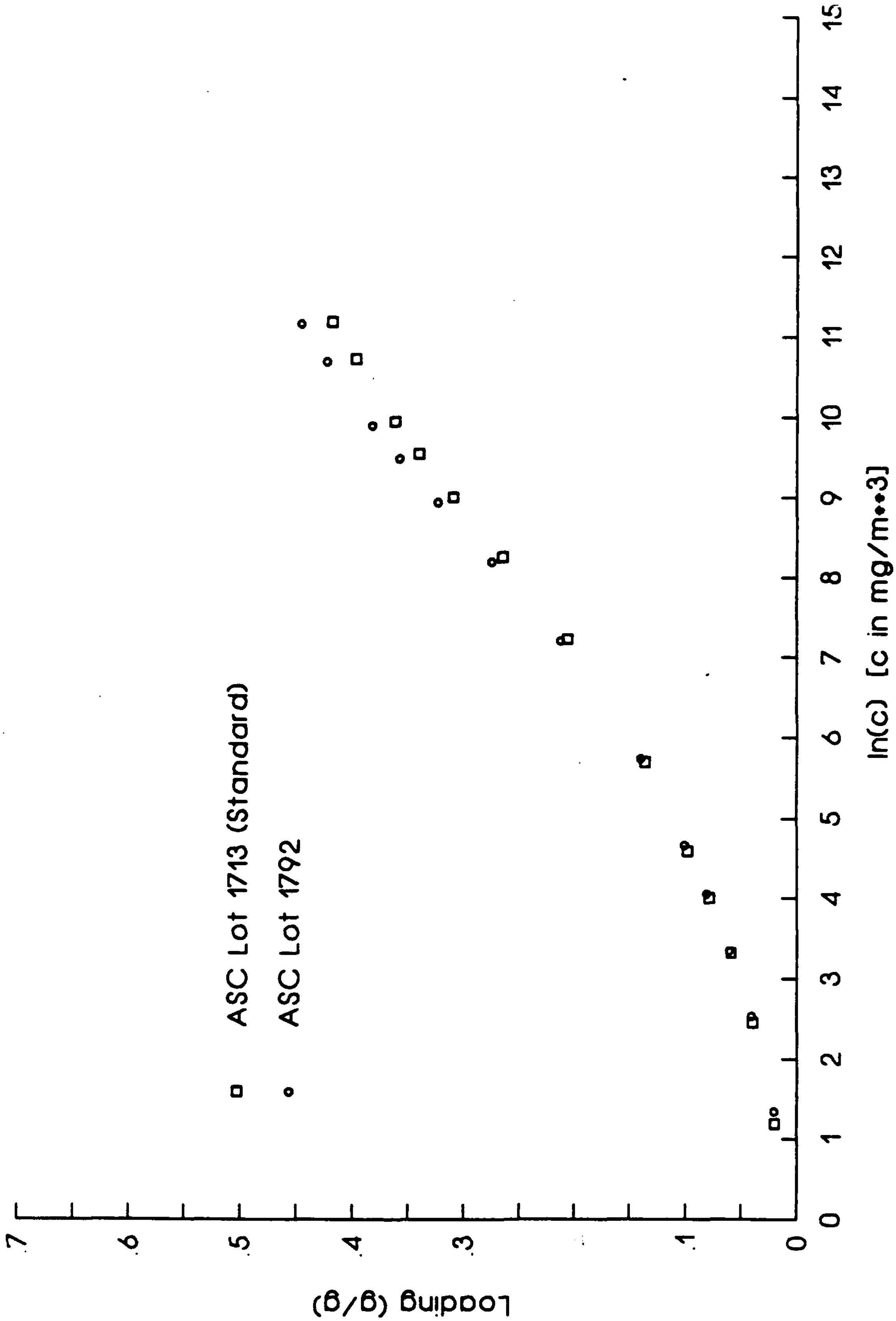

Figure B-6. CFC-113 Isotherms
ASC Whetlerite Lots 1713 and 1792 at 298 K

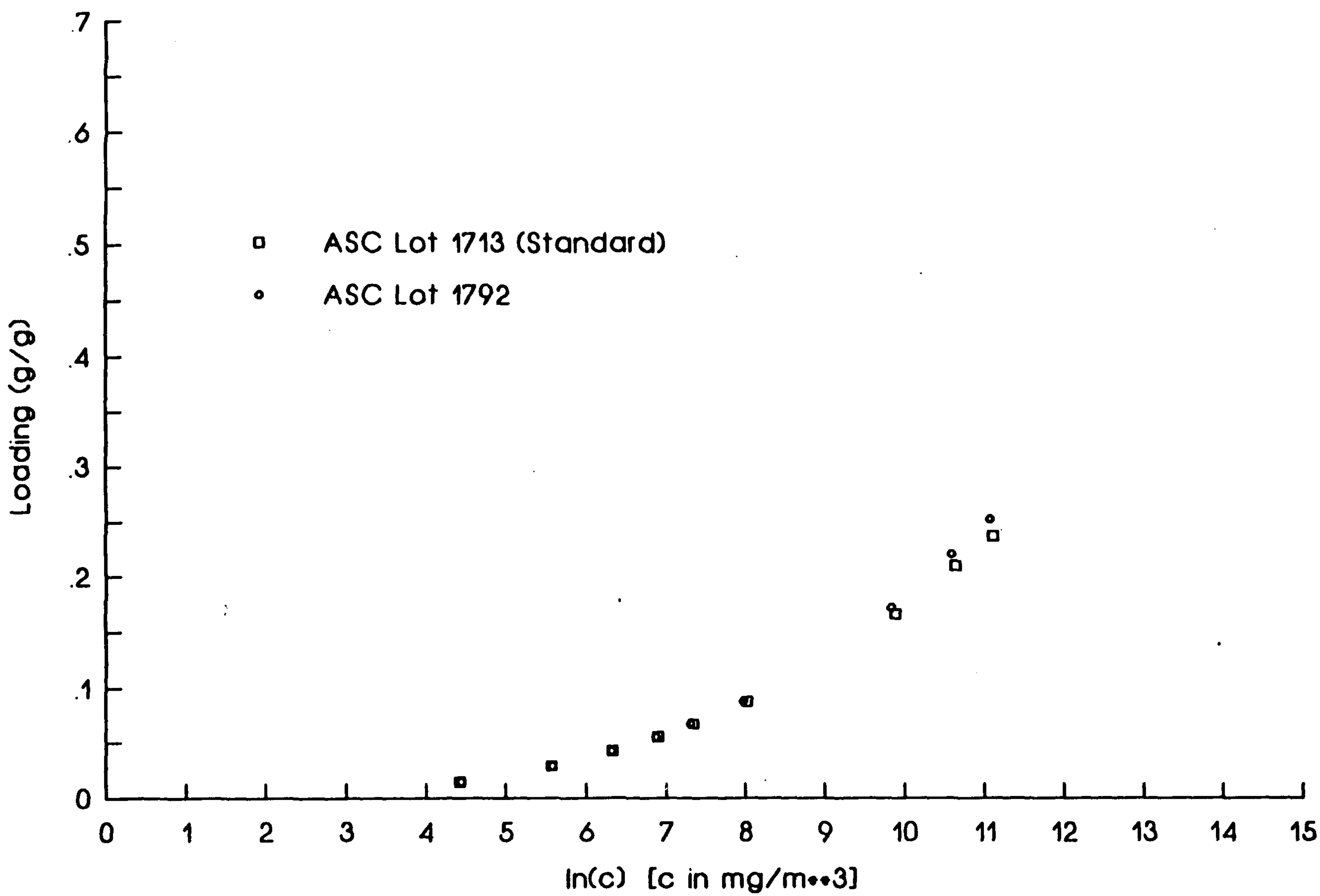

Figure B-7. **CFC-113 Isotherms**
ASC Whetlerite Lots 1713 and 1792 at 348 K

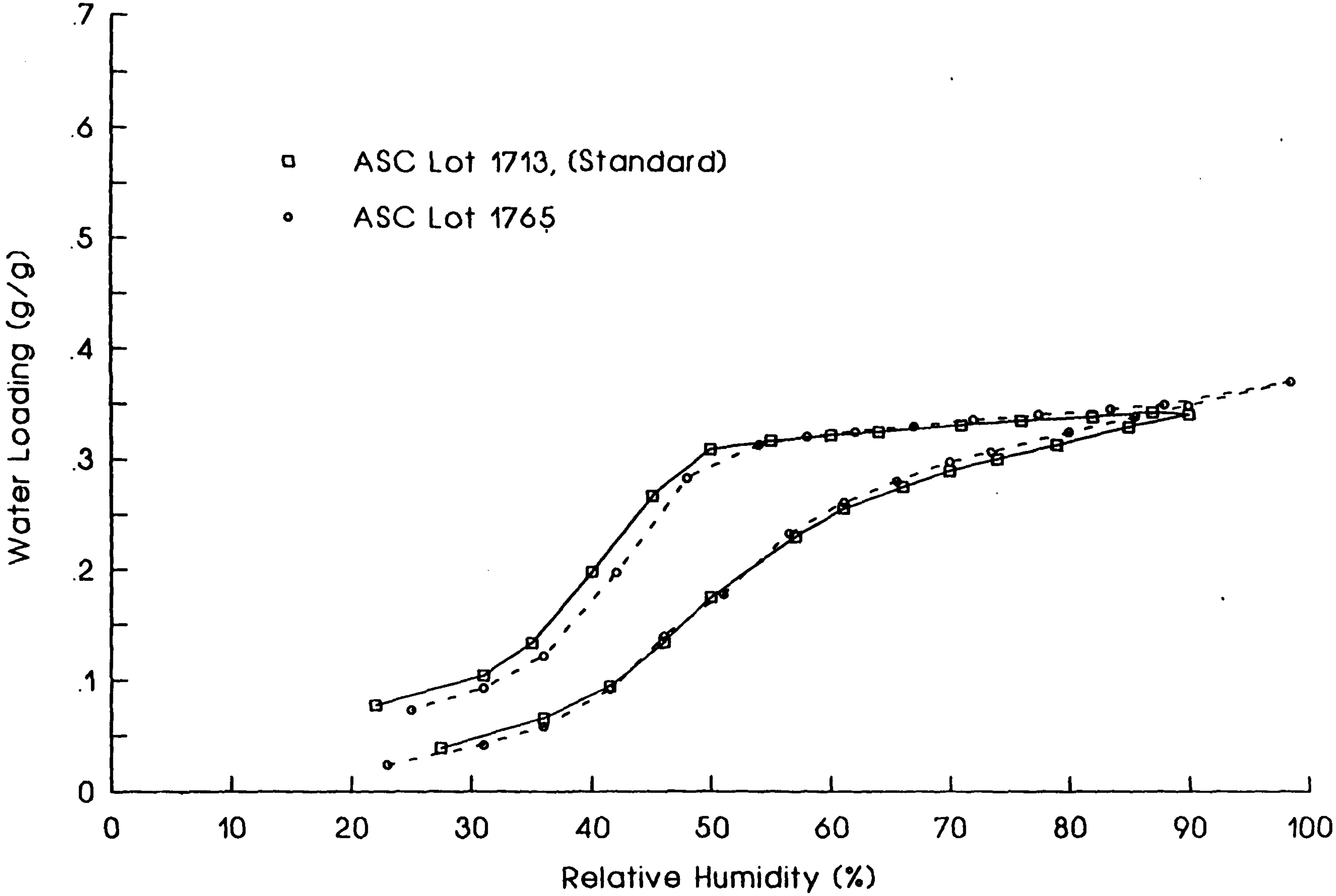

Figure B-8. ASC Whetlerite Lots 1713 and 1765

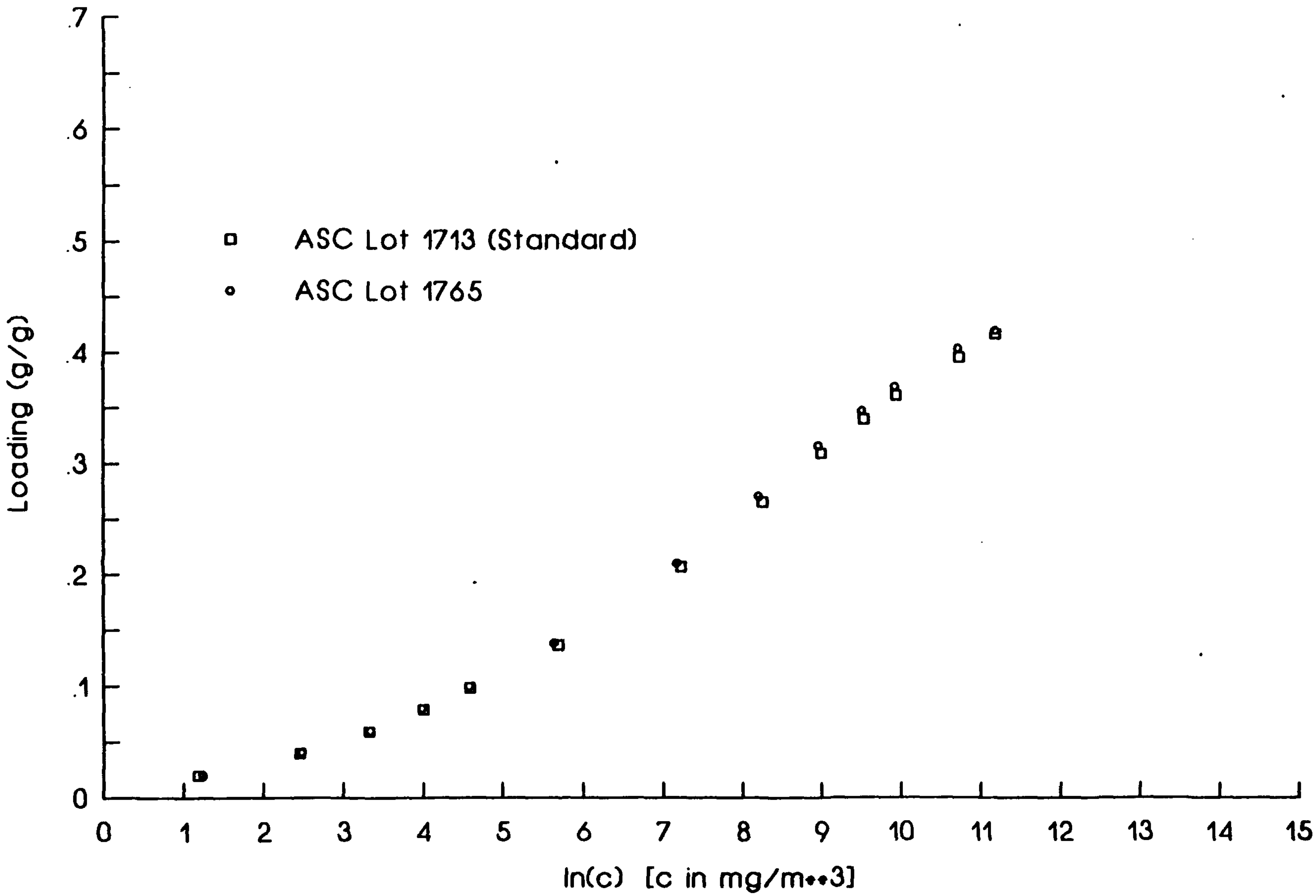

Figure B-9. **CFC-113 Isotherms**
ASC Whetlerite Lots 1713 and 1765 at 298 K

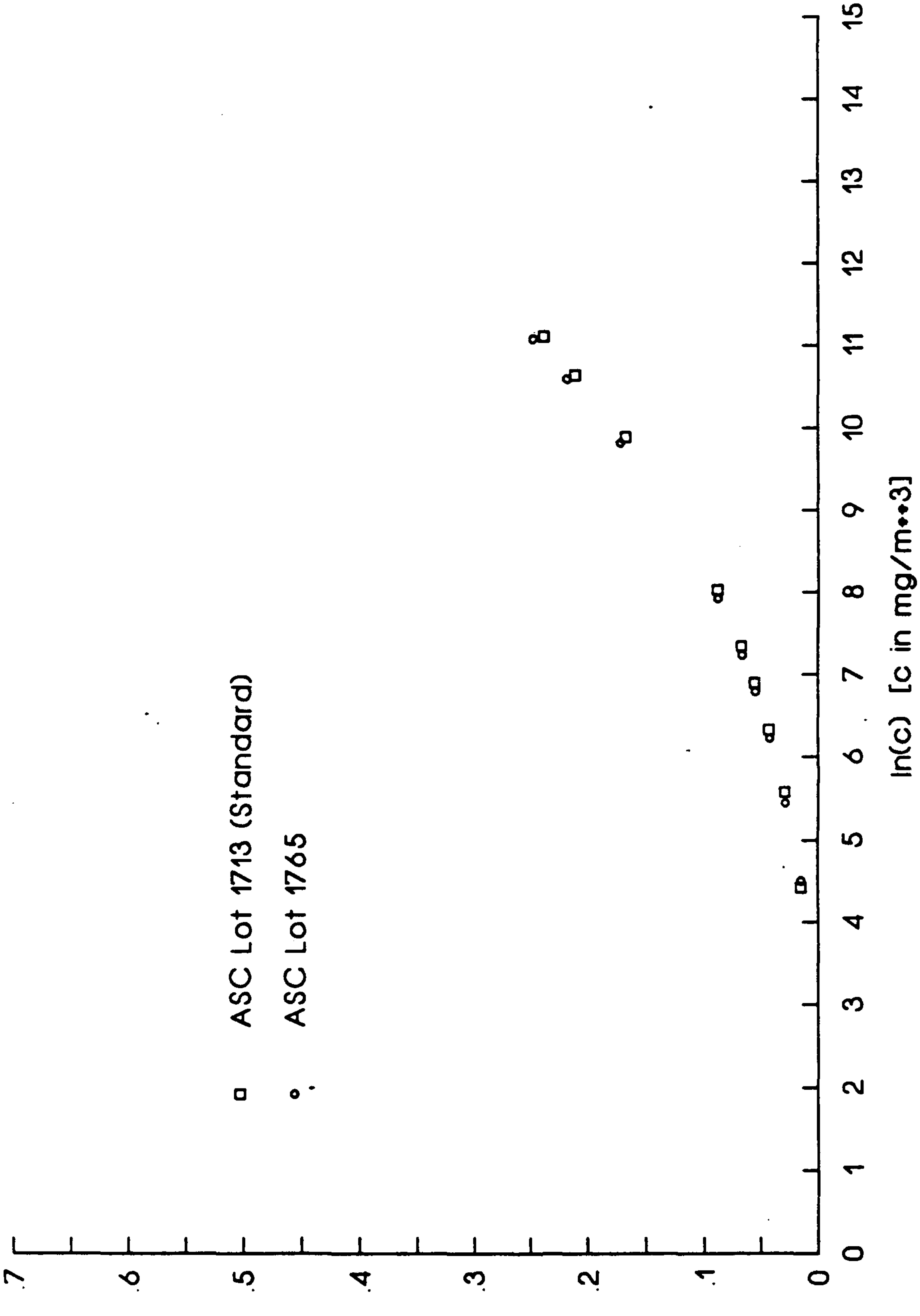

Figure B-10. CFC-113 Isotherms
ASC Whetlerite Lots 1713 and 1765 at 348 K

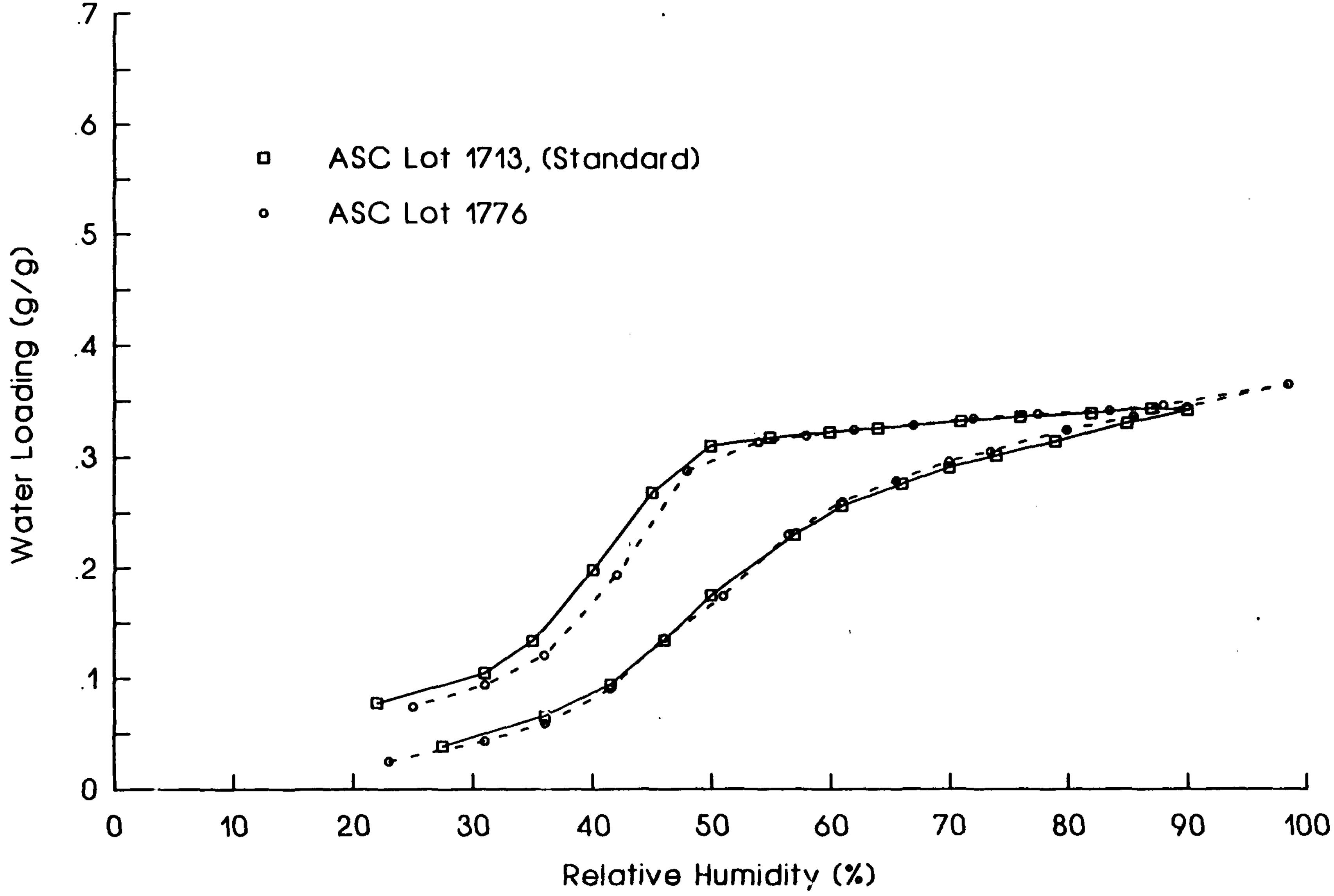

Figure B-11. ASC Whetlerite Lots 1713 and 1776

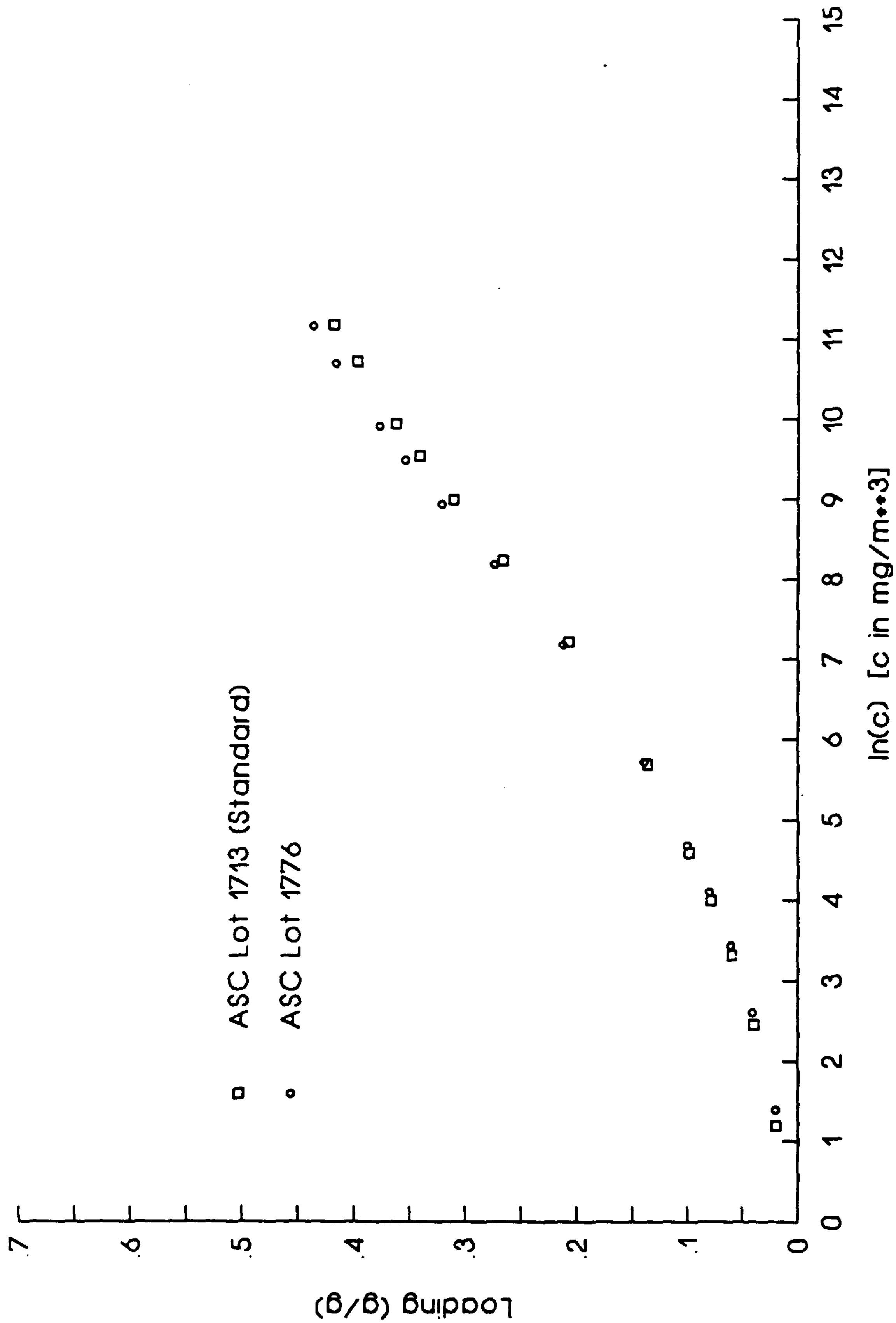

Figure B-12. CFC-113 Isotherms
ASC Whetlerite Lots 1713 and 1776 at 298 K

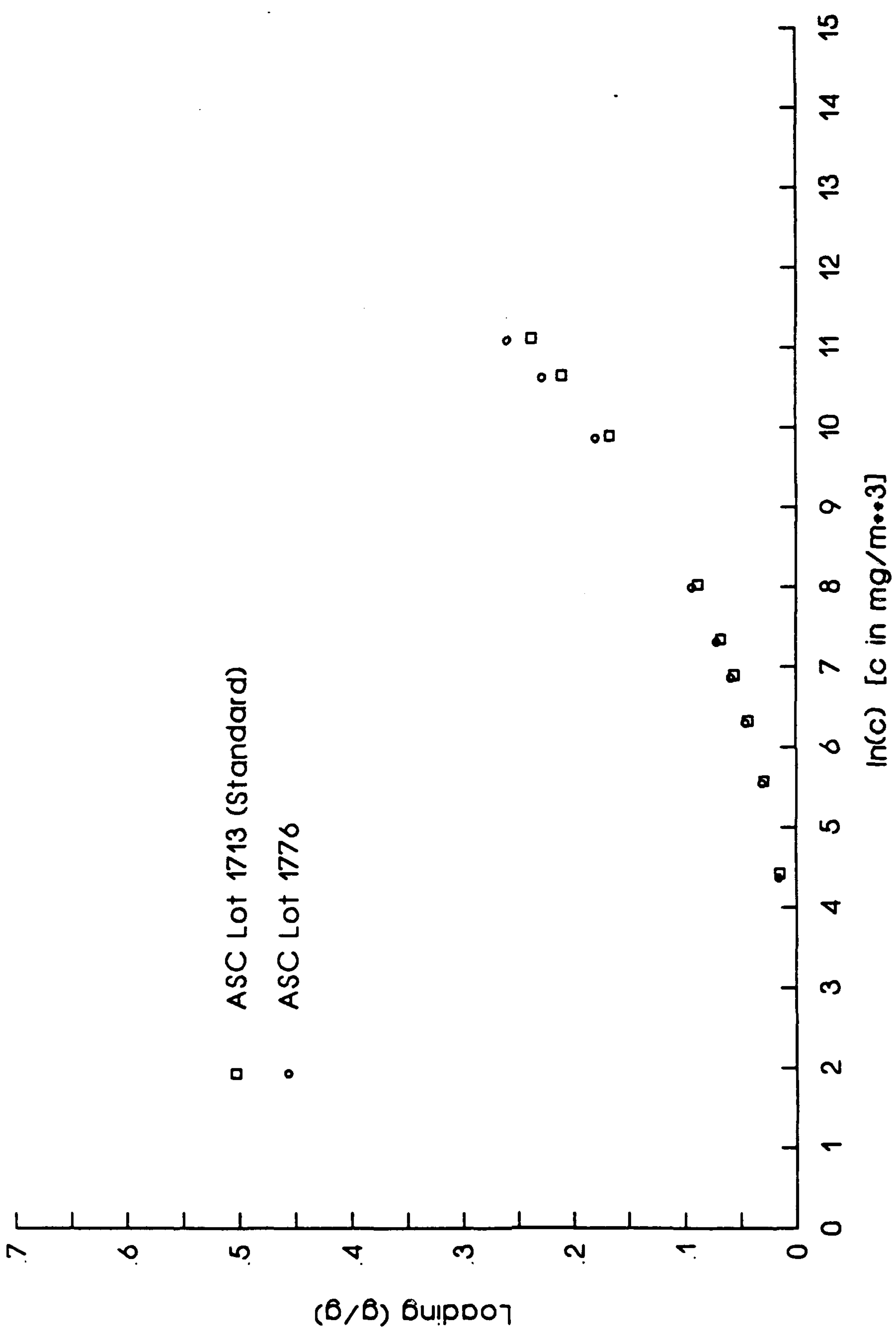

Figure B-13. **CFC-113 Isotherms**
ASC Whetlerite Lots 1713 and 1776 at 348 K

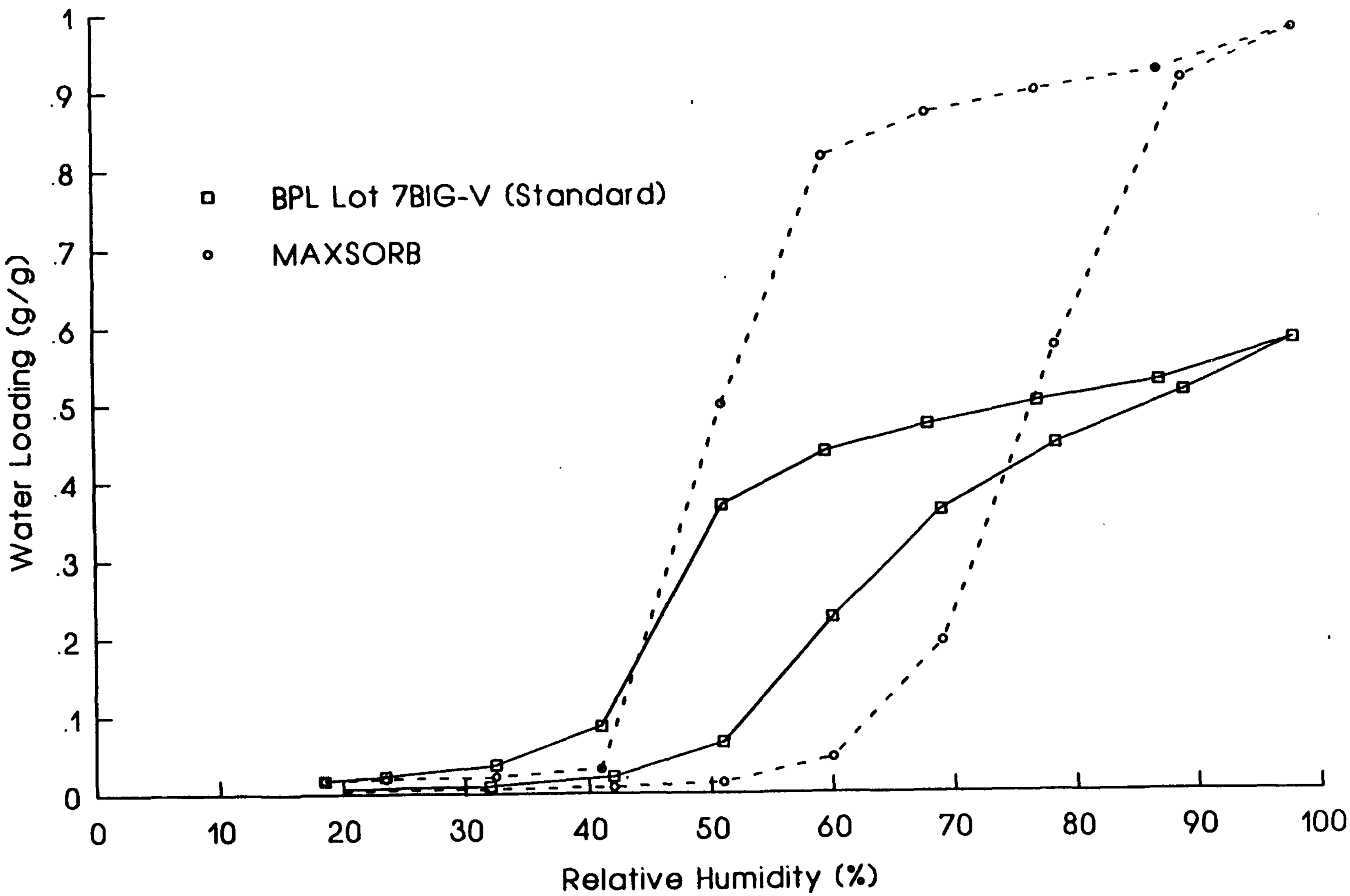

Figure B-14. BPL Lot 7BIG-V and MAXSORB

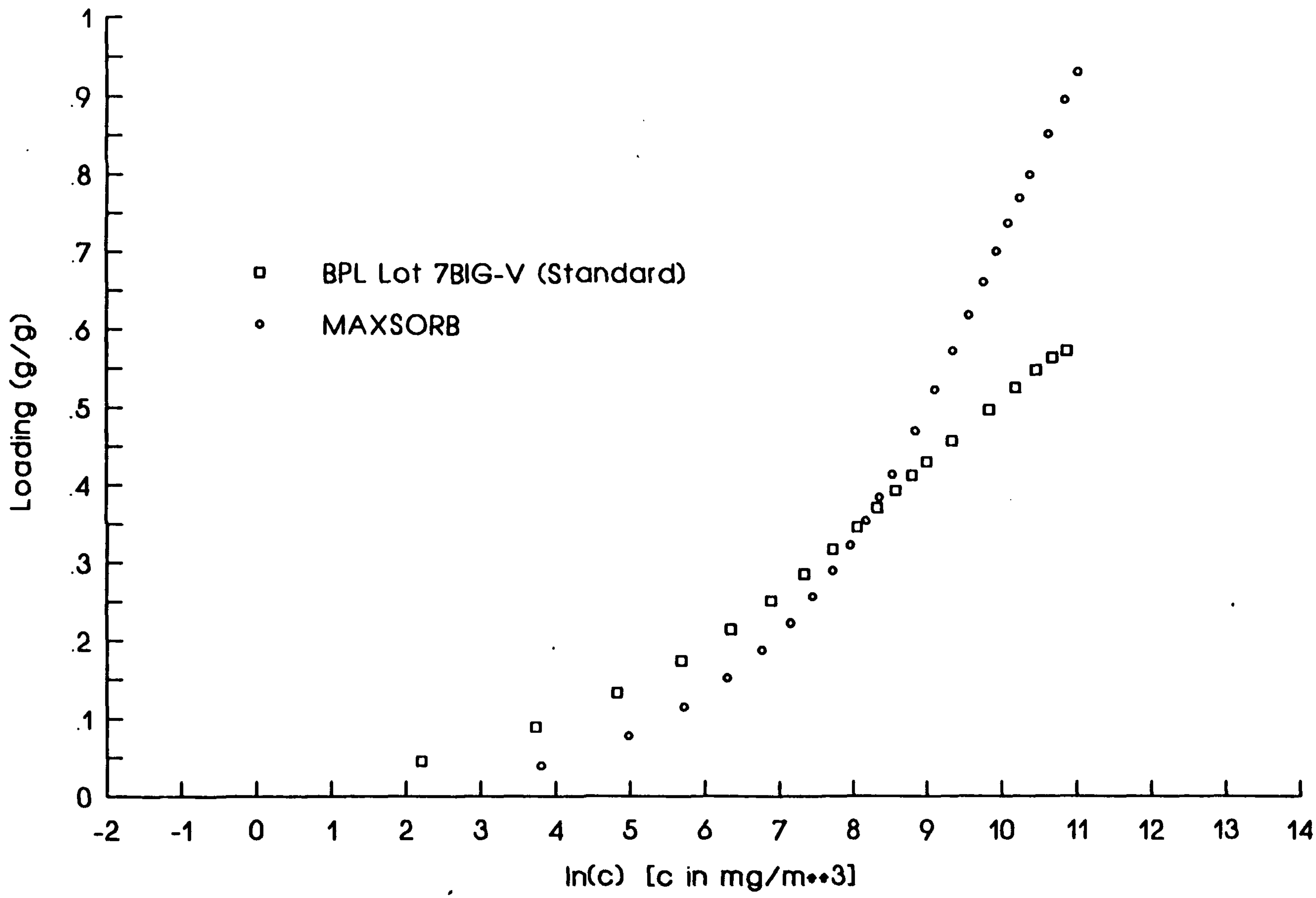

Figure B-15. CFC-113 Isotherms
BPL Lot 7BIG-V and MAXSORB at 298 K

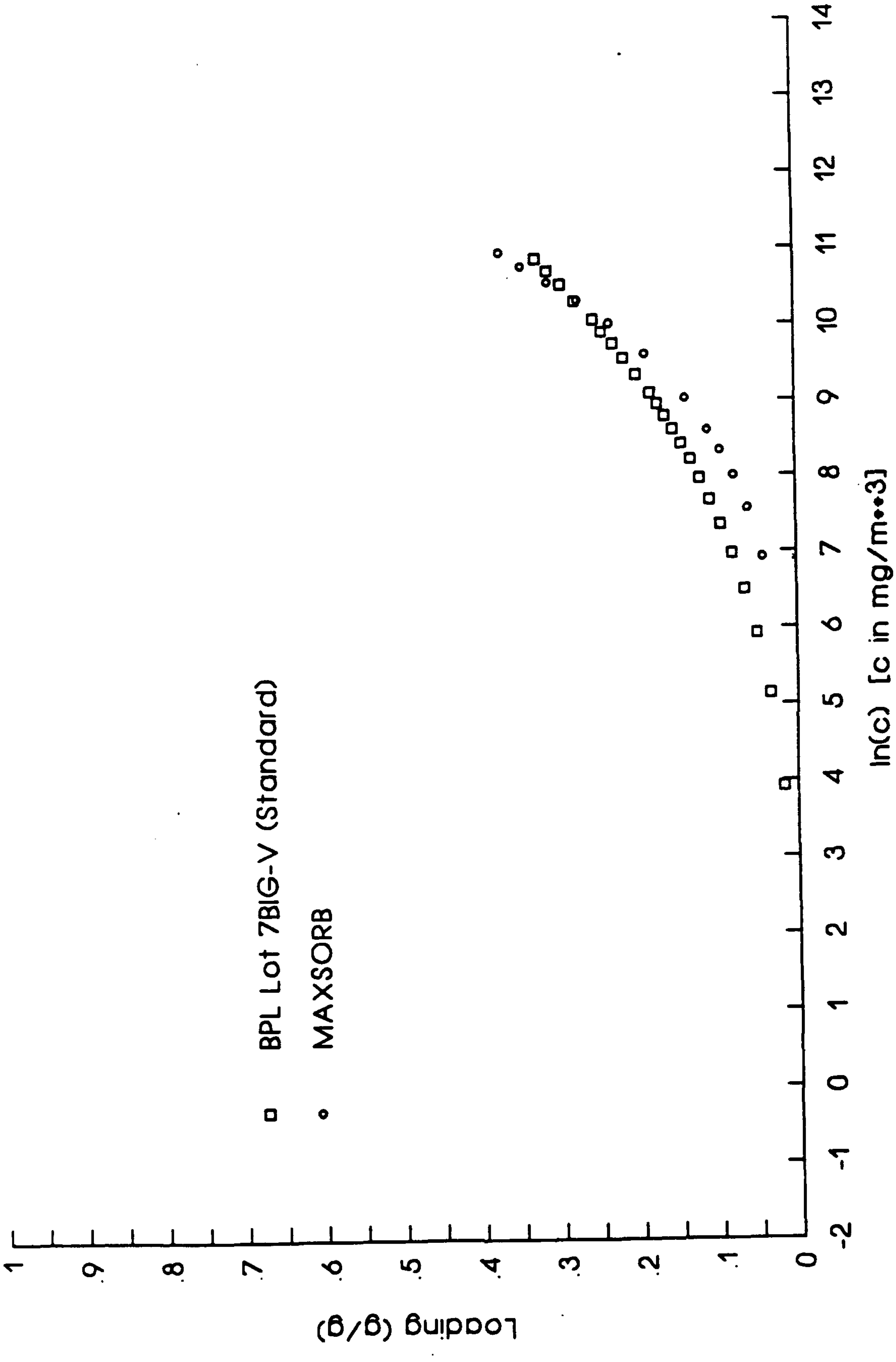

Figure B-16. CFC-113 Isotherms
BPL Lot 7BIG-V and MAXSORB at 348 K

COMPARATIVE LOADINGS FOR CFC-113 ISOTHERMS AT 298 AND 348 K

298 K

Carbon Sample	2,000 mg/m**3	60,000 mg/m**3
Standard (ASC Lot 1713)	.2734	.4128
ASC Lot 1765	.2706	.4209
ASC Lot 1761	.2663	.4317
ASC Lot 1776	.2733	.4364
ASC Lot 1792	.2754	.4457
MAXSORB	.3078	.928
BPL Lot 7BIG-V	.3174	.5745

348 K

Carbon Sample	2,000 mg/m**3	60,000 mg/m**3
Standard (ASC Lot 1713)	.0909	.2481
ASC Lot 1765	.0881	.2473
ASC Lot 1761	.0914	.256
ASC Lot 1776	.0937	.2595
ASC Lot 1792	.0886	.2532
MAXSORB	.0779	.3724
BPL Lot 7BIG-V	.1082	.3263

APPENDIX B