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ABSTRACT

Progress that has been made in the field of spectrophotometry of molten fluoride salts is summarized in this report. The high-temperature cell assembly which was designed and fabricated for use in this work is described, as are the various types of sample containers that have been used. Spectra of nickel fluoride, cobalt fluoride, chromic fluoride, and uranium tetrafluoride in LiF-NaF-KF (46.5 - 11.5 - 42 mole per cent) are presented.

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STATUS REPORT--SPECTROPHOTOMETRY OF MOLTEN FLUORIDE SALTS

J. P. Young

In this report the progress that has been made in the studies which are being carried out to investigate the possibilities of spectrophotometric measurements in molten fluoride salts is summarized. The equipment that was developed for making spectral studies in molten fluoride salts is discussed and the results that have been obtained to date with the apparatus are presented.

The solvent which has been considered to date has been the eutectic of LiF-NaF-KF, "Flinak," (46.5 - 11.5 - 42 mole per cent) which melts at approximately 460°C. Other molten fluoride solvents will be studied as the work progresses. The immediate objectives of the present program are to obtain spectra and absorption coefficients of uranium, iron, chromium, nickel, cobalt, vanadium, and molybdenum in the various oxidation states that are believed to be in existence in the molten fluoride salt mixture.

Apparatus

The high-temperature cell assembly, which was designed and fabricated for spectral work with molten fluoride salts,(7) is shown in Figure 1. The assembly is used with a Cary Recording Spectrophotometer, Model 14-M. The Cary spectrophotometer can be converted from normal to high-temperature use in less than a minute. The furnace is composed of two fused-silica plates, wound with platinum wire, which are so positioned in a solid, nonmetallic, insulating block (Lavite) that the fluoride salt container can be placed between the heaters. This cavity is also of proper size to accomodate a normal 1-cm spectrophotometer cell. The furnace block is surrounded by "Fibrefrax" insulation and enclosed in a copper cylinder which is water cooled. The whole assembly is suspended from a plate which fits the top of the sample compartment of the Cary spectrophotometer. Suitable light ports allow complete transmission of the available light through the high-temperature cell assembly. The small removable lid permits access into the furnace. The various ports in this lid are for the introduction of thermocouples, an inert gas and for other functions.

The two heating elements are connected in series so that it is possible to heat the cavity between the heaters to a temperature of 800°C within 30 minutes. To attain this temperature, a current of seven amperes is supplied by applying 26 volts to the heaters. No automatic control of the temperature of the furnace has been incorporated into the design of the high-temperature cell assembly as yet. This could easily be done by including proper electronic components, but the nature of the present phase of this project does not seem to warrant this modification. Manual control of the voltage supplied to the heater elements is quite adequate to maintain control of the temperature of the furnace within ± 10 per cent. The water jacket on the side of the copper cylinder keeps the outer shell of this assembly below room temperature. Above 700°C some thermal radiation is noted through the quartz window, and only the temperature of the removable lid rises to the extent of about 60 to 80°C.

Several types of sample containers have been used to contain molten fluoride salts for spectral work.(7) A transmission cell was fabricated from crystalline magnesium oxide, MgO, by ultrasonic machining techniques and then rendered transparent by lapping and polishing. This cell is useful for spectrophotometric measurements down to wavelengths of 300 to 320 mμ. Crystalline magnesium oxide, MgO, is inert to molten alkali fluorides and fairly inert to alkali fluoride mixtures which contain fluorides of transition elements with low atomic weights, such as iron and nickel, in low concentrations. Magnesium oxide is not inert to all fluoride salts; for example, uranium or zirconium fluorides attack this oxide quite readily.

Confining the molten fluoride salt as a pendant drop is another possible approach(6) to the problem of suitably containing these corrosive melts for spectral investigation. Although it is recognized that the optical problems associated with a lens-shaped drop of liquid are indeed formidable, spectrophotometric measurements of pendant drops of molten fluoride salts appear to be feasible. A ring of platinum wire seems to be an ideal pendant drop container; however, a ring of reasonable size, 0.5 to 0.7 cm in diameter, must be maintained in a horizontal plane in order to hold a stable drop of liquid. The physical arrangement of the Cary spectrophotometer is such that pendant drops can be maintained only in a vertical position. To hold a pendant drop of liquid in this position it is necessary to confine the liquid in a closely wound coil of platinum wire. A later innovation of the coil which has proved to be extremely useful is the replacement of the coil with a platinum tube, 3/16-inch in diameter and 1-cm long.

The proposed optical arrangement of a spectrophotometer designed specifically for pendant drops is shown in Figure 2. The drop, contained in a ring, is positioned at the focus of a light beam as shown. With such an arrangement the optical effects of a lens-shaped drop of sample are minimized (and for all practical purposes, eliminated). The optical design of the Cary Model 14-M spectrophotometer is such that the light beam passes horizontally through the sample compartment and is focused there. By locating the pendant drop in the focal plane of the light beam and by allowing only the light which passes through the sample to impinge on the detector, a semblance of the ideal optical design shown in Figure 2 can be obtained. In order to achieve a suitable optical balance when the Cary spectrophotometer is used as a pendant drop spectrophotometer, it is necessary to mask out about 90 to 95 per cent of the reference beam of the instrument. This is done with light absorbing screens. The design of the Cary spectrophotometer is such that it can be operated adequately under these modified conditions.

The advantages of using a pendant drop of molten fluoride salts for spectrophotometric measurements are many. Corrosion effects of the fluoride ion are definitely minimized. The containers are easily cleaned by dipping them in boiling sulfuric acid for a few minutes. The range of wavelengths available for spectral study of pendant drops should be limited only by the transmission of the solvent. It does not appear that this ideal limit has been achieved as yet with the Cary spectrophotometer, but spectral responses of molten fluoride solutions have been obtained from 2.5 μ down to 250-260 mμ. The containers are easily filled by immersing them in a liquid and then withdrawing the sample. The length of the light path through the solution poses a rather serious problem with this type of container since the size of the drop is not reproducible and is somewhat difficult to measure. For this reason, quantitative spectrophotometric determinations cannot be made until suitable methods can be devised for determining the thickness of the pendant drop. Several ways of performing this task are being considered, such as the use of internal standards, photographing the drop (for use with platinum ring samples only) and geometrical calculations concerned with the platinum tube samples when the weight and density of the sample solution contained in the tube are known.

Some of the various containers for molten fluoride salts, a didymium glass bead in a platinum ring, a platinum coil, platinum ring, and crystalline magnesium oxide cell, are shown in Figure 3. Each of the containers designed to support a pendant drop is attached to a ceramic rod, as shown in the drawing. For spectral studies, this ceramic rod is positioned and extends through the center port of the lid of the cell assembly. The container is maintained in proper position by a suitable clamp which is attached to that portion of the ceramic rod that protrudes through the lid.

The didymium glass bead was used to check the feasibility of obtaining spectra of a pendant drop of sample. Aqueous solutions of neodymium chloride have also been used for this purpose in the various pendant drop containers. A typical example of the spectral response that was obtained for the didymium glass bead is shown in Figure 4. The bead was contained in the cold, high-temperature furnace assembly. The spectrum of a didymium glass plate is also shown in Figure 4 for comparison. Over the region of wavelengths from 350 to 620 mμ, the spectra are essentially identical, both with respect to wavelength of maximum absorbance and to the ratio of the various peaks heights P_i to the height of the peak at 530 mμ. These data are shown in Table I.

Table I

Comparison of the Absorption Spectra of a Didymium Glass Plate and Bead

Instrument: Cary Recording Spectrophotometer, Model 14 M

Wavelength of Absorbance Maximum, mμ		Ratio of Peak Heights P_i/P_{530} mμ x 10^3		
Plate	Bead	Plate (A)	Bead (B)	Difference (B-A)
530	529	-	-	-
527	525	858	850	- 8
514	513	587	599	+ 12
482	480	495	519	+ 24
479	478	514	529	+ 15
473	472	487	495	+ 7
447	445	398	385	- 13
442	438	423	407	- 16
432	431	386	375	- 11
403	402	152	145	- 7

The magnitude of the peaks is different due to the difference in thickness of the two samples. The optical response shown in the bead spectra from 620 to 700 mμ arises from the use of the Cary instrument. This effect can be eliminated by making various instrumental adjustments.

Absorption Spectra of Molten Fluoride Salts

The spectra of Flinak and NiF_2 in Flinak at 500°C are shown in Figure 5. Both of these spectra were obtained with the melt in the MgO cell (internal dimension, 0.5 cm). The optical cut-off of the MgO cell is observed at approximately 310 mμ. Nickel fluoride exhibits a maximum absorbance at 434 mμ, and a very insensitive, broad peak at 850 mμ. Gruen(4) has reported that $Ni(NO_3)_2$ in molten $LiNO_3$-KNO_3 (184°C) exhibits peaks at 425 and 775 mμ. Boston and Smith(2) have reported that $NiCl_2$ (as a complex anion) in molten LiCl-KCl at temperatures up to 600°C has four peaks between 512 and 695 mμ and a tremendously sensitive peak at 260 mμ. Aqueous nickel solutions in 1 M $HClO_4$ exhibit peaks at 390 and 710 mμ.(1)

The absorbance index of NiF_2 at 434 mμ is of the order of 20 to 30 based on moles of Ni per 1000 g of solution. This expression of sensitivity will be referred to as a molal absorbance index.

In Figure 6 is shown the spectrum of CoF_2 in Flinak at a temperature of 500°C. The melt was contained in a platinum tube. The actual path length of the solution was of the order of 0.5 cm. Cobalt fluoride exhibited two peaks, at 510 and 580 mμ. The molal absorbance index of the CoF_2 peak at 580 mμ is probably of the order of 10 or 20. Gruen has reported that $Co(NO_3)_2$ in molten $LiNO_3$-KNO_3 at 184°C has one peak at 560 mμ.(1)

The spectrum of CrF_3 in Flinak at a temperature of 650°C is shown in Figure 7. The sample was contained in a platinum tube. Two peaks are observed, at 445 and 685 mμ. In order to dissolve CrF_3 it was necessary to keep the solution fairly hot, and at the present time the actual concentration of chromium in the melt is not known. From the data obtained, it is expected, however, that the molal absorbance index will be above 10. In aqueous solution the chromium (III) has two peaks, at 410 and 575 mμ.(3)

The spectral response of UF_4 in Flinak at 550°C is shown in Figure 8. The melt was contained in a platinum coil. Well defined peaks were observed for UF_4 at 420, 470, 522, 600, and 1100 mμ. From an inspection of Figure 8 a discrepancy is to be noted in the spectra of uranium at two concentrations within the wavelength region from 550 to 700 mμ. It appears probable that the peak for 10 per cent U at 600 mμ is in error and that the actual peak is at 670 mμ, as shown in the spectrum for a 1 per cent solution of uranium. More work is planned to resolve this question. The 1100-mμ peak for tetravalent uranium is well known and corresponds to a UCl_4(5) peak in LiCl-KCl.

The spectra of these solutes and other solutes of interest will be studied more critically, as suitable experimental techniques are evolved, in order to obtain accurate values for spectrophotometric sensitivity. Studies are also planned to investigate the various parameters involved in these spectral measurements, such as the effect of temperature and solvent composition. Possible methods for measuring the temperature of molten fluoride salts more accurately in the high-temperature cell assembly are being evaluated. The temperatures reported in this section were obtained by applying empirical corrections to a measurement of the temperature of the Lavite furnace block and are only approximate, ± 50°C.

The possibility of using various chromogenic reagents as a basis for possible colorimetric determinations in molten fluoride salts is being considered. Obviously the chromogenic reagent (probably organic in nature) would have to be thermally stable up to temperatures of at least 460°C. One class of compounds which meets this specification is the phthalocyanines. Phthalocyanine and metal-phthalocyanine dyes are thermally quite stable. They sublime only at temperatures exceeding 500°C. They are not selective reagents; however, phthalocyanine exhibits two peaks at 660 and 700 mμ, and when a metal such as copper, magnesium, iron, etc. is present, the two former peaks disappear and only one peak is observed at 680 mμ. Although magnesium-phthalocyanine is thermally stable, it is not chemically stable and is decomposed by cold sulfuric acid. Phthalocyanine is not soluble in Flinak or even LiCl-KCl; however, possible additions to the molecule are being considered to make the resultant compound more soluble. Magnesium-phthalocyanine was found to be soluble in molten phthalic anhydride; however, as shown in Figure 9, apparently the magnesium compound is decomposed in this solvent to yield free phthalocyanine. This decomposition is indicated by the recognizable phthalocyanine spectra. When cuprous ion was added to the same melt, copper-phthalocyanine was formed as indicated by the spectrum. These and other possible high-temperature chromogenic reagents will be studied further as time and possibilities will allow.

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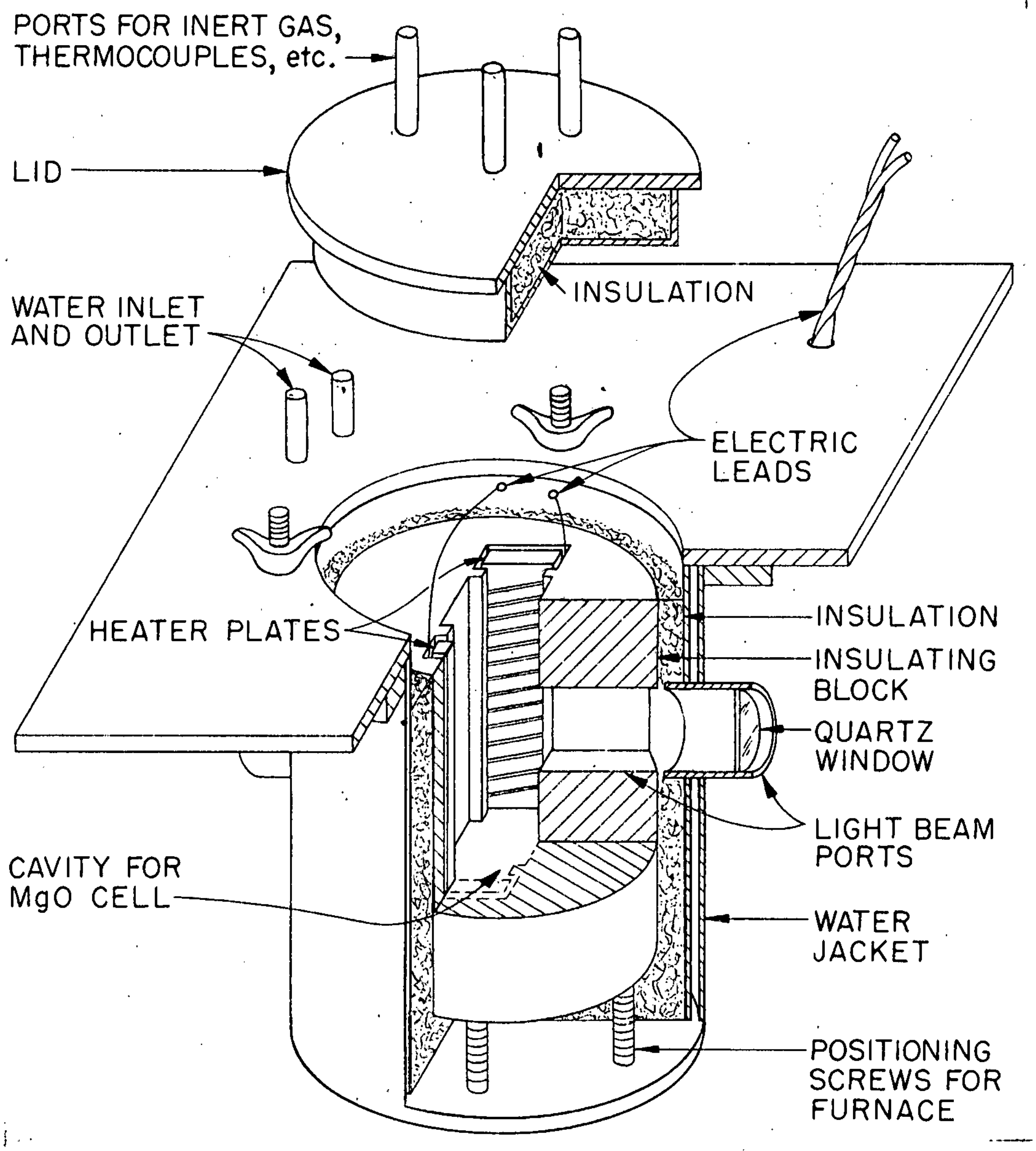

Figure 1

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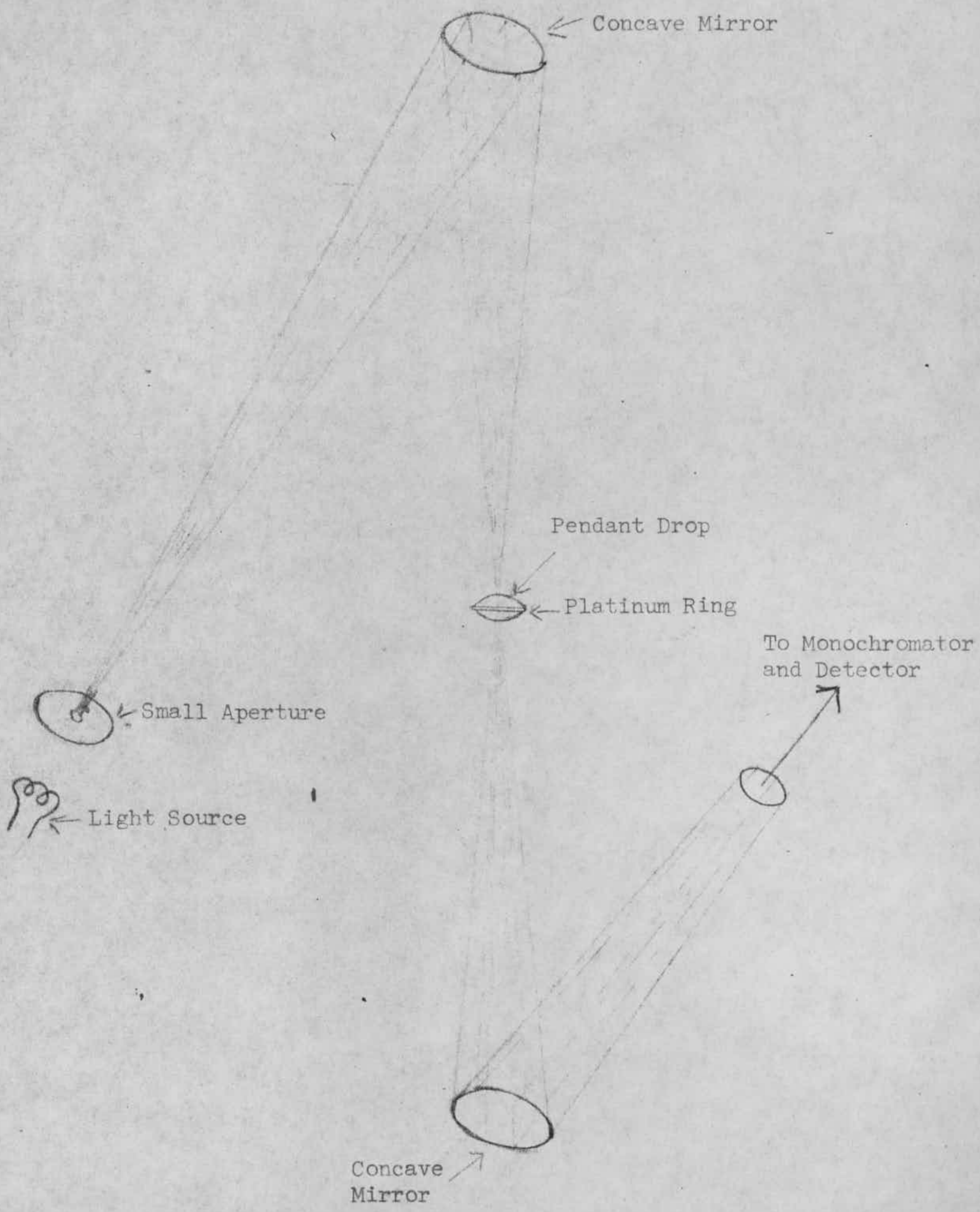
Figure 2

Proposed Optical Design for Pendant Drop Spectrophotometer



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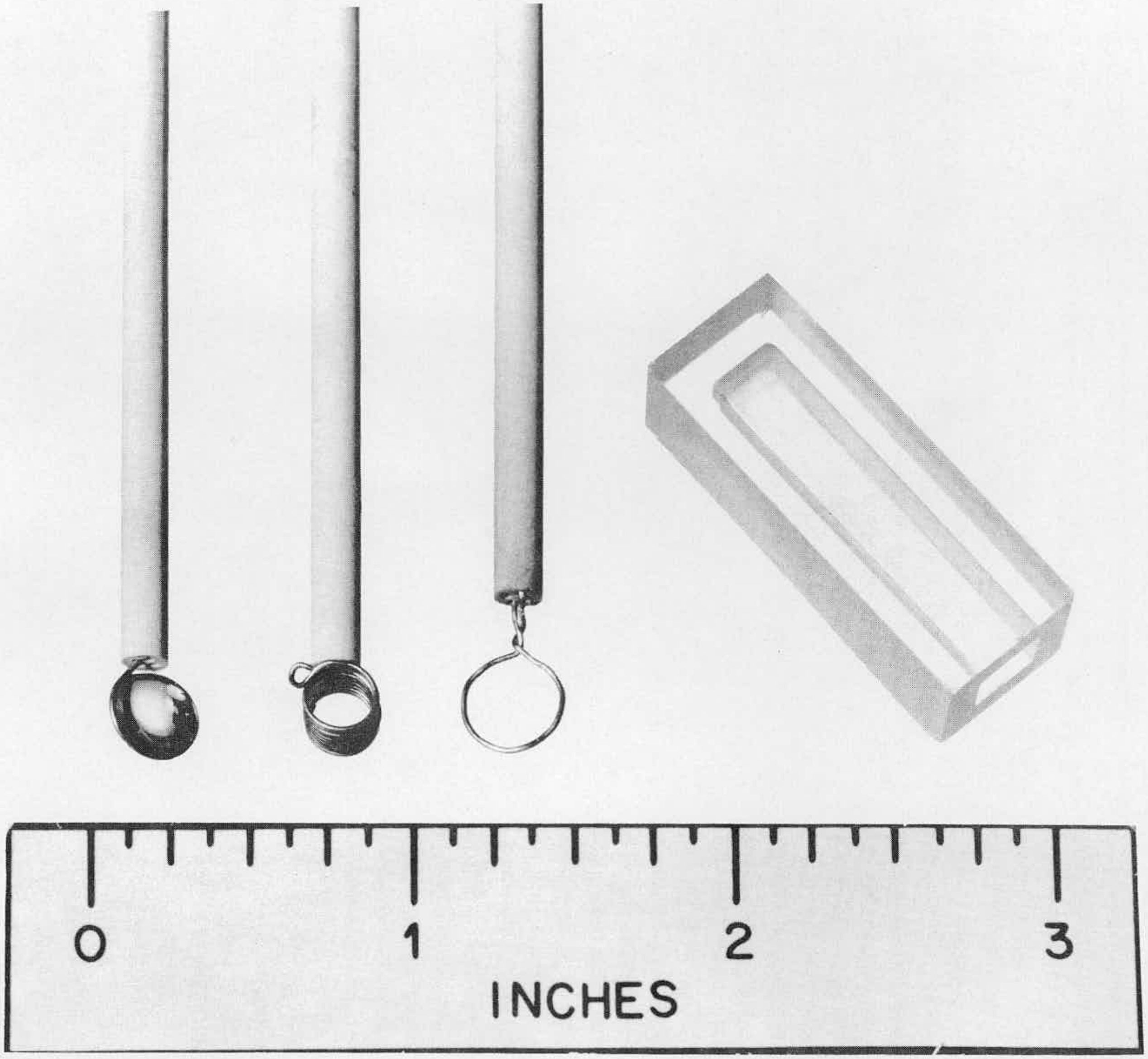

Figure 3. Sample Containers for use in Spectrophotometric Studies.

Figure 4. Absorption Spectra of Didymium Glass

Instrument: Cary Recording Spectrophotometer, Model 14 M
Reference Medium: Air

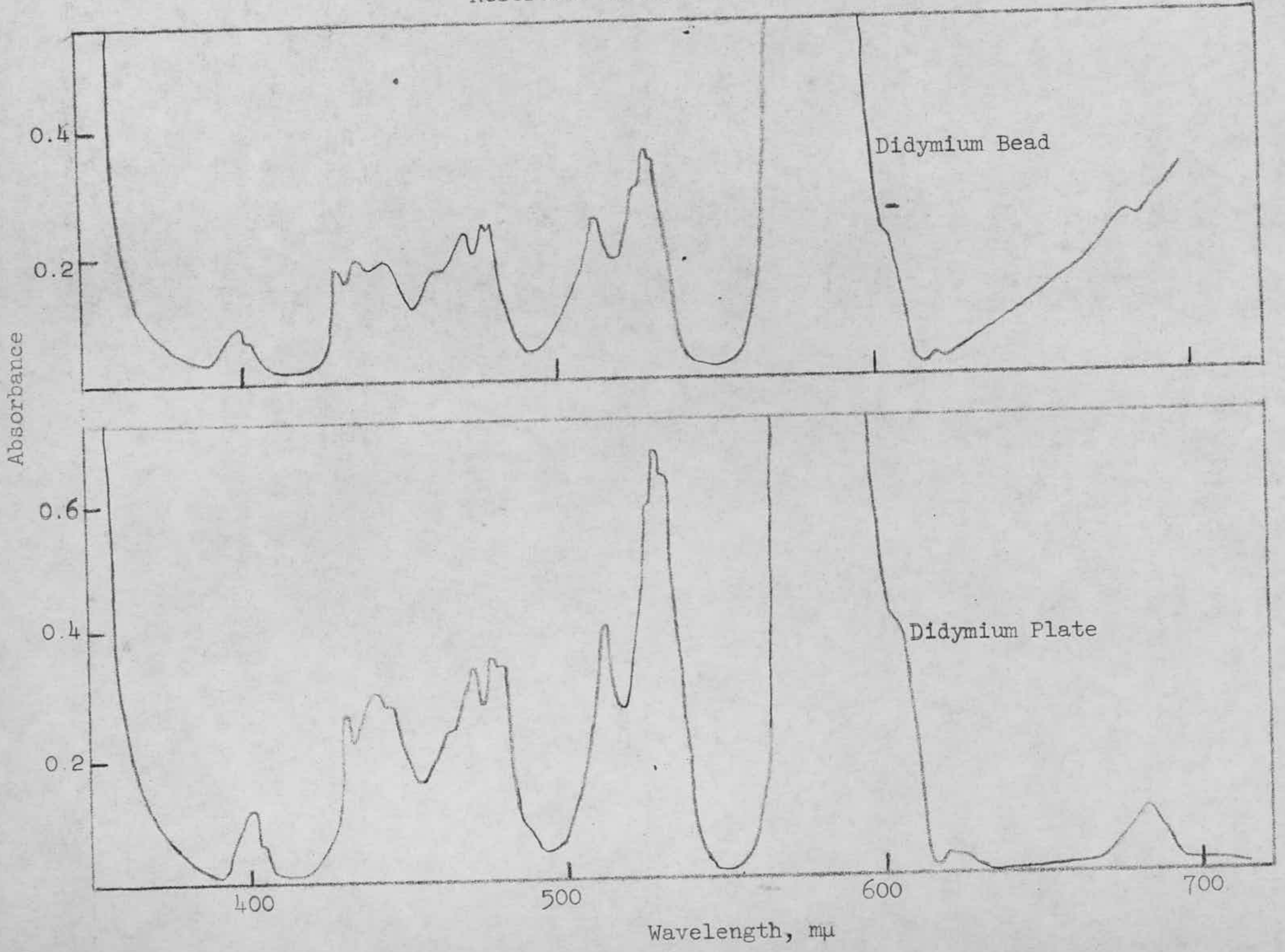

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Figure 5. Preliminary Spectra of NiF_2 in LiF-NaF-KF

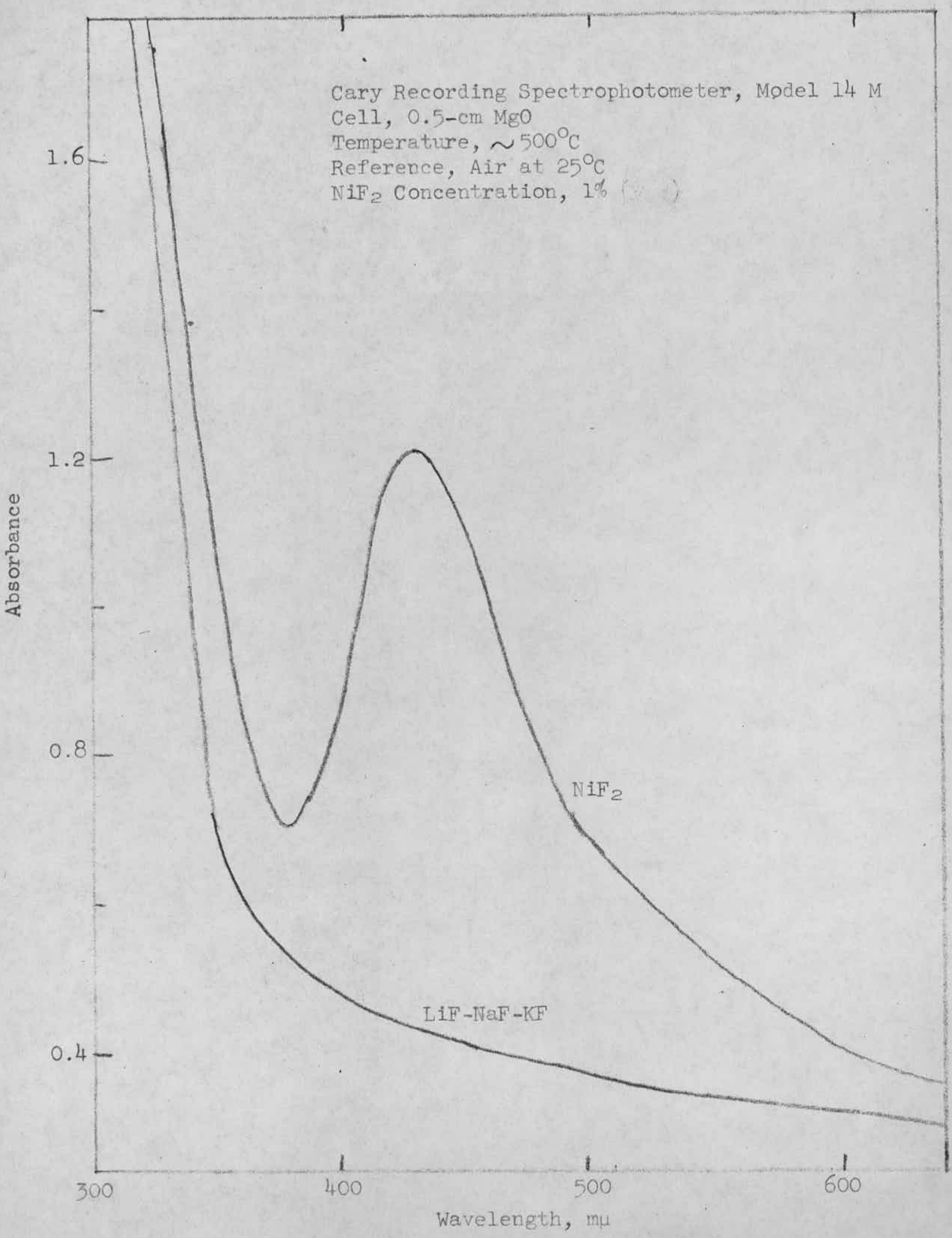

Figure 6. Preliminary Spectra of CoF_2 in LiF-NaF-KF

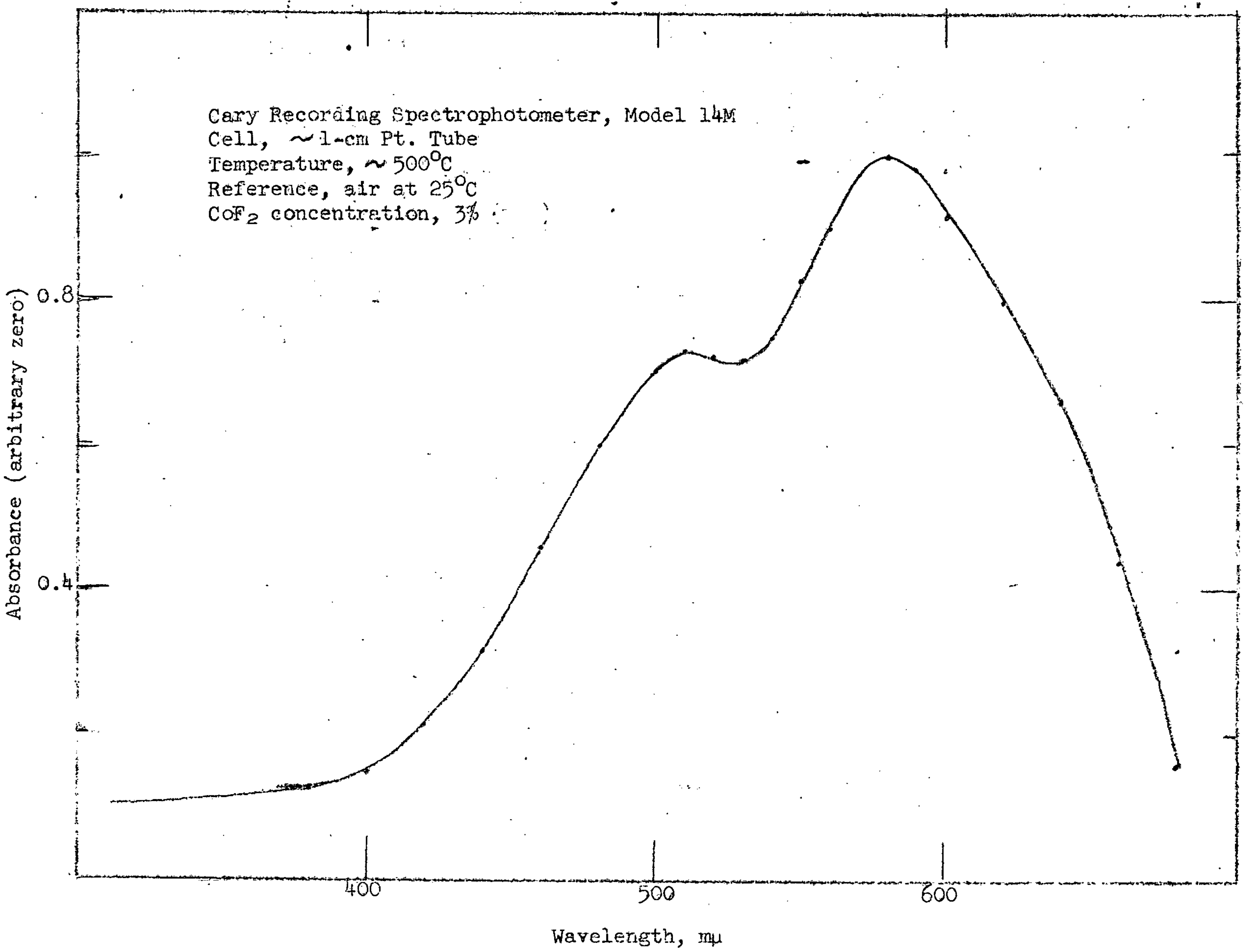

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Figure 7. Preliminary Spectra of CrF_3 in LiF-NaF-KF

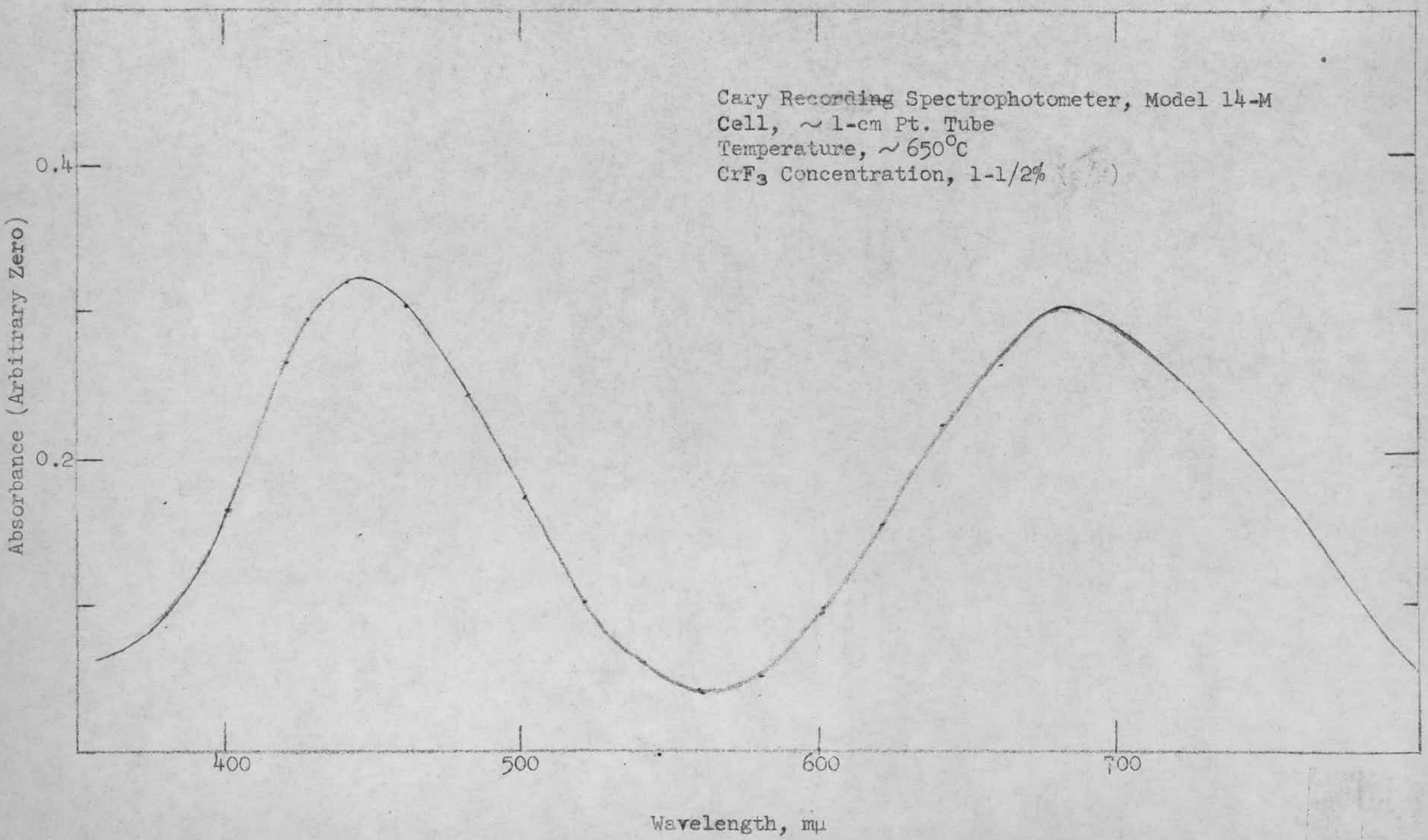

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Figure 8. Preliminary Spectra of UF_4 in LiF-NaF-KF

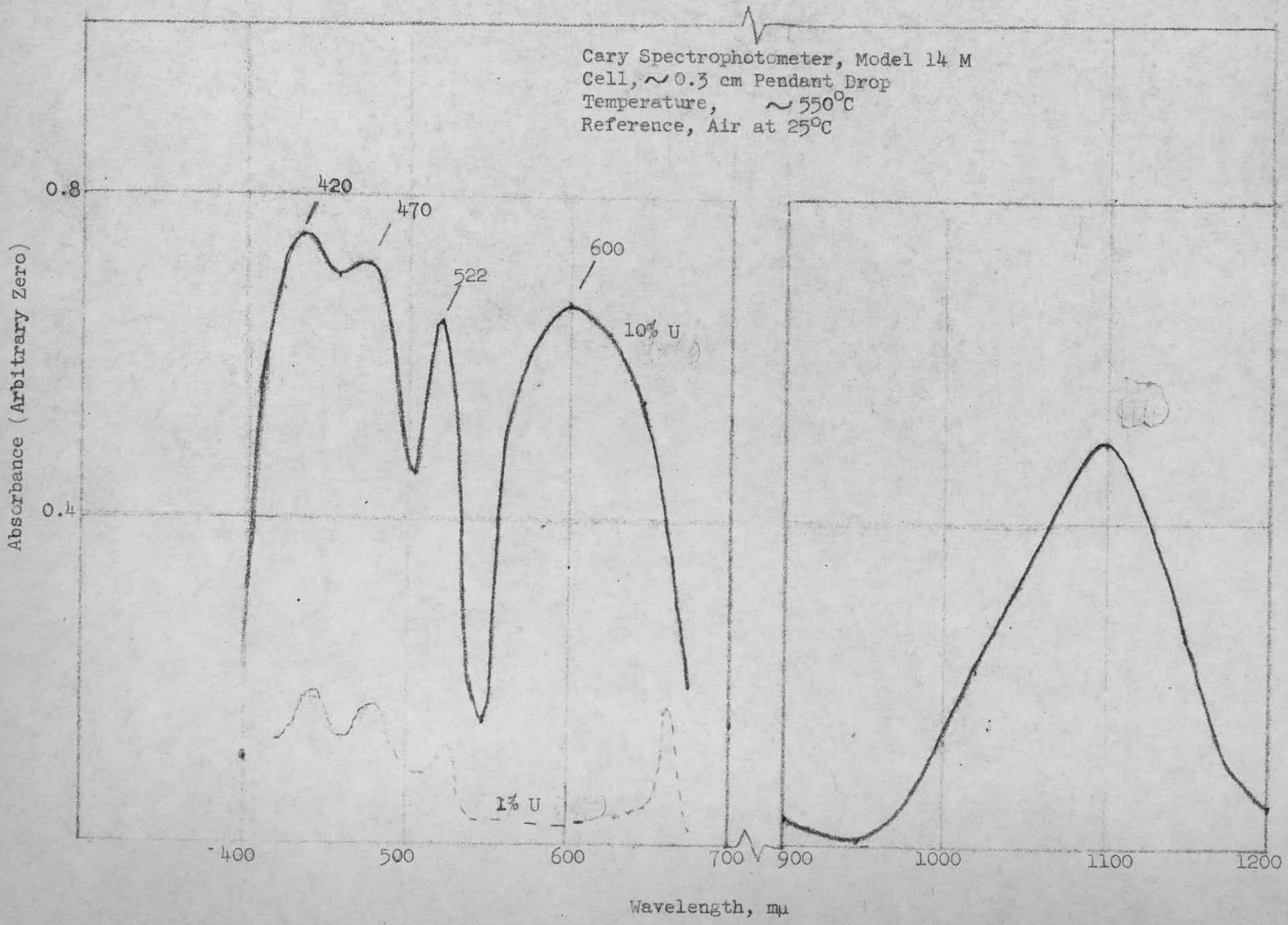

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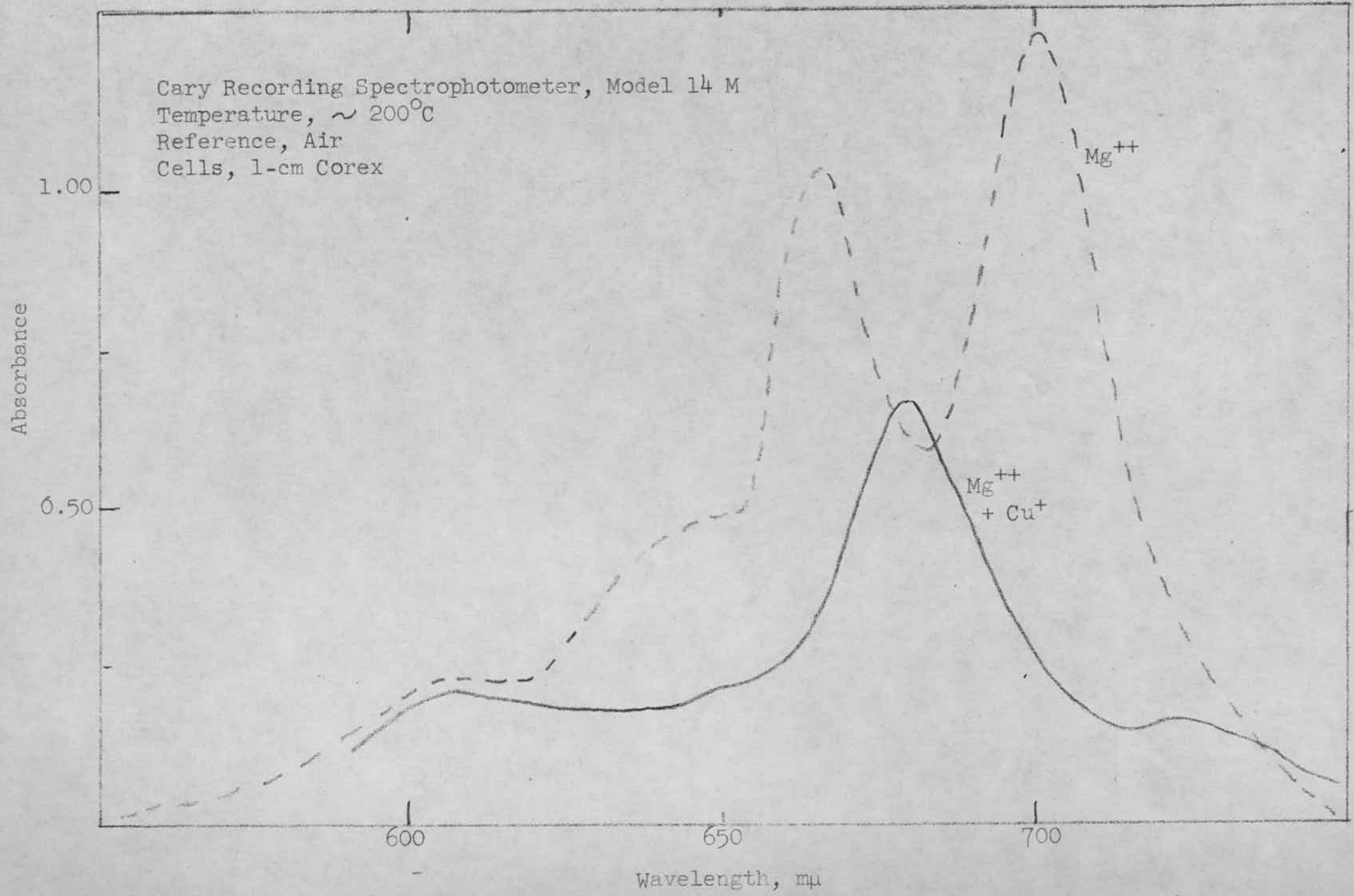
Figure 9

Absorption Spectra of Some Metal Phthalocyanines in Molten Phthalic Anhydride



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