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MINES BRANCH

OTTAWA

Mines Branch Investigation Report IR 69-24

A STUDY OF THE SENSITIVITY OF THE DIFFERENTIAL
THERMAL ANALYSIS EQUIPMENT IN THE PHYSICAL
CHEMISTRY SECTION, MINERAL SCIENCES DIVISION,
MINES BRANCH, OTTAWA

by

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MINERAL SCIENCES DIVISION

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SUMMARY OF RESULTS

A study was undertaken of the sensitivity of the differential thermal analysis equipment in the Physical Chemistry Section, Mineral Sciences Division, or its ability to resolve or separate the peaks on the thermograms corresponding to reactions that occur close together in temperature. Synthetic mixtures of potassium or lithium sulphate with quartz were used to generate the required thermograms. It was found that, except for extreme cases, the performance of the equipment was satisfactory and could probably be improved by some modifications in the design of the sample holder.

Details are given in an Appendix of experiments conducted to elucidate the reason for certain apparently spurious peaks that were recorded under the experimental conditions employed. The trouble was traced to contamination of the sample holder by previous samples.

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INTRODUCTION

The Differential Thermal Analysis (DTA) equipment in use in the Physical Chemistry Section, Mineral Sciences Division, Mines Branch, Ottawa, has been fully described in an earlier report⁽¹⁾. In order to assess the ability of this DTA equipment to produce separate peaks on the differential curve of a thermogram corresponding to reactions that occur very close together in temperature without resorting to dilution of the sample with alumina or other diluent, test runs were made using two mixtures of substances that have reversible crystal transformations. One mixture consisted of potassium sulphate and quartz in equi-molar proportions and the other of lithium sulphate and quartz, also in equi-molar proportions. The materials used in the experiments were powders prepared from Merck reagent-grade potassium sulphate crystals, Baker and Adamson reagent-grade lithium sulphate crystals and Brazilian quartz crystals. The temperatures reported for the crystal transformations of these substances are: K_2SO_4 588°C; Li_2SO_4 575°C; quartz ($\alpha \rightarrow \beta$) 573°C. To ensure that the lithium sulphate was in the anhydrous state for the tests, it was found necessary to calcine it at 300°-400°C and then to keep it stored in a desiccator as it readily converted to the monohydrate when exposed to the atmosphere. No such precaution was necessary with the potassium sulphate since it is non-hygroscopic.

EXPERIMENTAL PROCEDURES AND RESULTS

The tests were conducted in a static air atmosphere and each series of runs was made at two different rates of temperature change. In one set of runs, the mixtures were cycled through the crystal inversions at heating and

(1) For references, see page 20.

cooling rates of 3 deg C per minute. In another set of runs, the mixtures were heated through the transition temperatures at 12 deg C per minute and then were allowed to cool at the natural cooling rate of the furnace which was approximately 7 deg C per minute at the transition points. The initial test runs were made in a palladium sample holder using a Pt vs Pt:13% Rh difference couple. The sample cavity of the sample holder, when packed in the usual manner, required about 595 mg of the K_2SO_4 - quartz mix and about 480 mg of the Li_2SO_4 - quartz mix.

The differential curve of the K_2SO_4 - quartz mix, recorded at the 3 deg per minute schedule, showed good peak separations on both the heating and cooling cycles with the greater separation occurring on the heating cycle. The curve of the Li_2SO_4 - quartz mix, however, on the same heating schedule, registered the quartz inversion peak as a slight bulge on the low-temperature side of the Li_2SO_4 transition peak, while, on the cooling portion of the cycle, the quartz inversion was completely obscured by the sulphate peak. At the faster temperature rate, the peak separation on the heating cycle of the K_2SO_4 - quartz mix was satisfactory although not as large as at the slower temperature rate, but, on the cooling cycle, the quartz peak appeared as a shoulder on the larger sulphate transition peak. In the case of the Li_2SO_4 - quartz mix at the faster temperature schedule, the quartz inversion endotherm was completely obscured by the sulphate transition peak on both heating and cooling cycles.

Runs were made at the fast and slow temperature rates on the K_2SO_4 - quartz mix in which an alumina sample holder of similar size and shape was substituted for the palladium holder. However, the peak separations obtained were not as large as those obtained with the metal sample holder. This result is probably due to the increase in peak areas caused in part by the lower conductivity of the alumina compared with palladium. The difference in heat capacity of alumina as compared with that of palladium metal would have a smaller contrary effect. The much larger K_2SO_4 peak would tend to spread out and merge with the relatively small quartz peak.

It therefore became clear that, in order to produce any separation of the quartz and sulphate inversion peaks on the differential curve of the Li_2SO_4 - quartz mix and to increase further the peak separation in the case of the K_2SO_4 - quartz mix, the metal sample holder would have to be used, and also that it would be necessary not only to reduce the weight of the sample, but to increase, as much as possible, the ratio of the surface area of the sample in contact with the sample holder to the weight of the sample. This would reduce the total amount of heat involved in the crystal transformations and, at the same time, increase the rate of heat flow to and from the sample. Accordingly, the sample weight of the mixtures used for further tests was reduced to 100 mg. This resulted in an increase of the sample - contact-area to sample-weight ratio from about 0.5 sq mm per mg to about 1.0 sq mm per mg, an increase of 2 times in the case of the K_2SO_4 - quartz mix, while for the Li_2SO_4 - quartz mix the increase was approximately 1 3/4 times.

The sample and reference-material cavities in the palladium sample holder are vertical cylindrical holes 0.25-in.-diam x 0.5-in.-deep and the differential couple junctions are inserted into the sample and reference material through holes drilled horizontally into the walls of the cavities halfway between the top and bottom. In order to keep the smaller weight of sample in a symmetrical position about the difference-couple junction, the bottom of the cavity was filled to the appropriate depth with -60 +100-mesh platinum spherical powder, on top of which was placed a 0.25-in.-diam. platinum foil disc, 0.01 mm thick. The sample was then packed around the difference-couple junction and covered with a platinum foil disc as above and the balance of the cavity filled with platinum spherical powder.

The crystal-transition peaks now obtained with the K_2SO_4 - quartz mix were sharper and the peak separation was greater than in the previous tests. This was shown, for example, during the cooling cycle at the faster temperature rate, for where the quartz peak had formerly appeared as a shoulder on the K_2SO_4 peak, there was now good separation. In the case of the Li_2SO_4 - quartz mix, during the heating cycle at the 3-degree/minute

temperature rate, the slight bulge on the sulphate peak indicating the quartz inversion now became a small distinct inflection. However, the quartz inversion still failed to show on the cooling cycle of the same run or on the heating and cooling cycles at the faster temperature rates.

A further series of tests was made in which the differential-temperature sensitivity of the system was increased about four-fold by replacing the platinum/rhodium-alloy difference couple with a chromel/alumel difference couple. Although this change resulted in sharper peaks of much higher amplitude, there was very little, if any, improvement in the separation of the quartz and sulphate endotherms of either mixture. However, the quartz inflection on the side of the Li_2SO_4 transformation peak on the 3-degree/minute heating cycle now became a small discrete peak, and a very slight, but noticeable, flexure appeared on the side of the sulphate peak at the quartz inversion temperature during the 12-degree/minute heating cycle.

Finally, the sample weight of the mixtures used for the tests was reduced still further to 50 mg and, by reducing the diameter of the sample cavity by 25% with a platinum sheet liner, the sample-contact area/sample weight ratio was increased to about 2.3 sq mm per mg. The thermograms obtained with this arrangement, however, showed only very slight improvement in the separation of the quartz and sulphate endotherms.

DISCUSSION AND CONCLUSIONS

The primary factors that would affect the magnitude of the separation of the quartz and sulphate crystal-inversion peaks on the DTA curves, irrespective of the equipment used, are: (a) the temperature difference between the inversions to be measured; (b) the relative sizes of the peaks (determined by the relative amounts of the substances present and the energies involved in their crystal transitions); and (c) the rate of heating or cooling during the test. In the case of the K_2SO_4 - quartz mix, the temperature difference between the inversions, 15°C , and the relative

sizes of the peaks, about 15 to 1, were favourable for obtaining good separation at the temperature rates that were used, even during the cooling cycles when the downward shift in temperature of the sulphate inversion peak was several degrees more than the downward shift of the quartz inversion peak. Figures 1 and 2 are photographic reproductions, reduced in size, of thermograms obtained with this mix (see Table 1). On the other hand, with the Li_2SO_4 - quartz mix, the difference in temperature between the crystal transitions, 2°C , and the relative sizes of the peaks, about 50 to 1, were unfavourable for obtaining satisfactory separation on the heating cycles, even at the 3-degree/minute temperature rate, while, during the cooling cycles, the downward temperature shift of the sulphate peak, which was considerably greater than the downward shift by the K_2SO_4 peak in the other mix, was such that the very small quartz peak was completely bridged by the very large Li_2SO_4 inversion peak. Figures 3 and 4 are photographic reproductions, reduced in size, of thermograms obtained with the Li_2SO_4 - quartz mix. It will be noted in these two figures that additional peaks of approximately the right size have been drawn in beside the differential curves to illustrate the correct temperature positions of the quartz inversion peaks relative to the sulphate transition peaks (see Table 1).

With respect to the DTA equipment used in this investigation, probably the most significant factors, in addition to the ones already mentioned, that would affect the resolution or separation of peaks that result from reactions that occur very close together in temperature during a DTA test are: the design of the sample holder, and the recorder-chart speed which, in this case, was fixed. The sample holder used for the tests proved to be adequate for this purpose in the case of the K_2SO_4 - quartz molar mixture, when used as described above, but, in the case of the Li_2SO_4 - quartz molar mixture, in which the crystal transitions were separated in temperature by only a couple of degrees and there was an extremely large disparity in the energies involved in the reactions, the results were not satisfactory. It is, therefore, concluded that, to provide the optimum conditions for an attempt to resolve the crystal-transformation peaks on the

thermiogram of the Li_2SO_4 - quartz mix, at any given rate of temperature increase or decrease, it would be necessary to increase the chart speed and to use a sample holder of high heat conductivity that was designed to hold only a few milligrams of sample, while providing as large a sample-contact area/sample weight ratio as possible.

Table 1

Conditions of Test for Thermograms

Figure	Figure 1	Figure 2	Figure 3	Figure 4
Sample	K_2SO_4 +quartz	K_2SO_4 +quartz	Li_2SO_4 +quartz	Li_2SO_4 +quartz
Sample weight	100 mg	100 mg	100 mg	100 mg
Heating rate	12 deg C/min	3 deg C/min	12 deg C/min	3 deg C/min
Cooling rate	7 deg C/min	3 deg C/min	7 deg C/min	3 deg C/min
Sensitivity*	30 μ v/inch	16 μ v/inch	70 μ v/inch	35 μ v/inch
Atmosphere	Static air	Static air	Static air	Static air

Difference couple - chromel vs alumel

Chart speed - 10 in./hr

Figures 1 to 4 follow on pages 8 to 11, respectively.

*Referred to original 10-in.-wide chart paper.

FIGURE 1

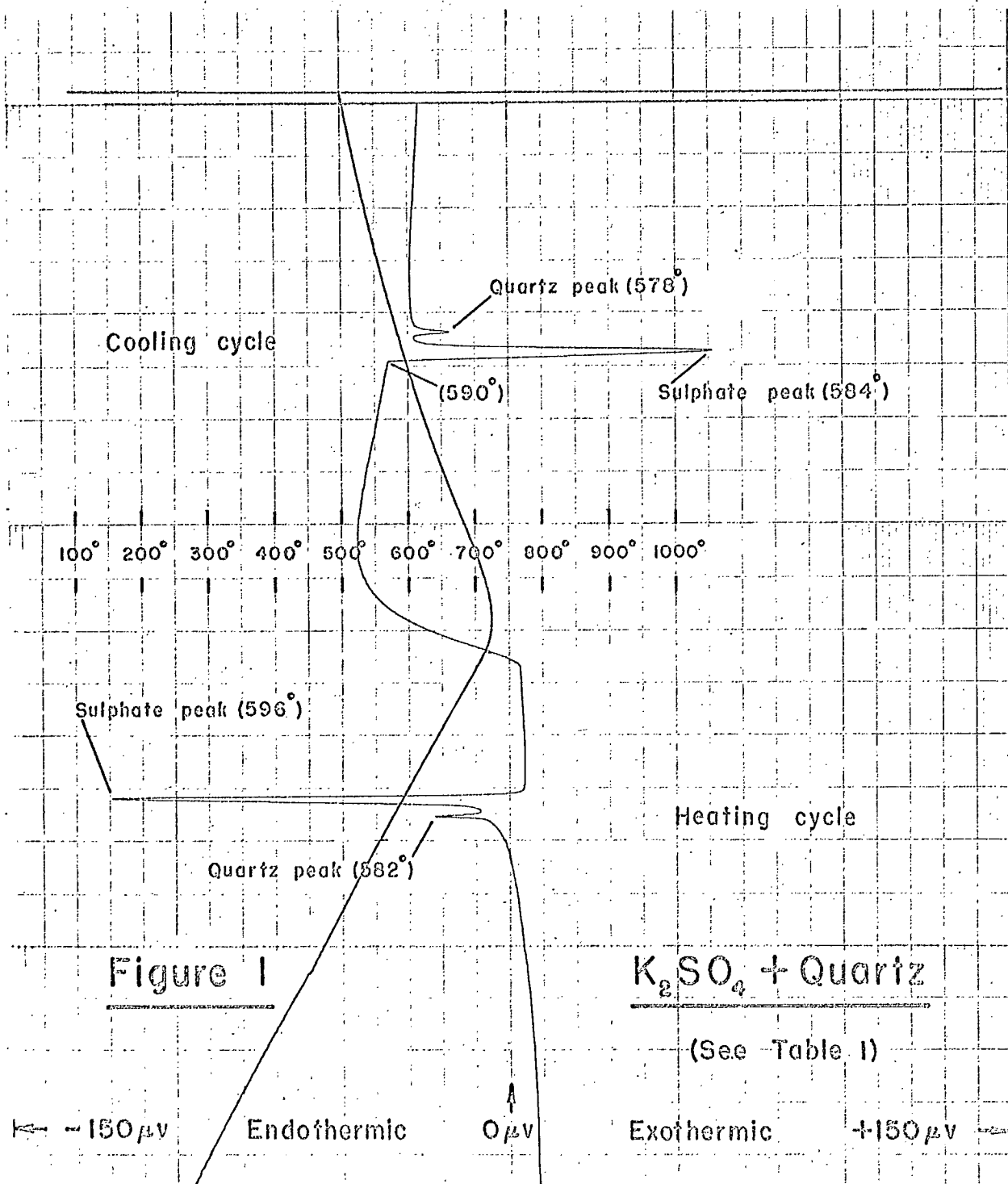


FIGURE 2

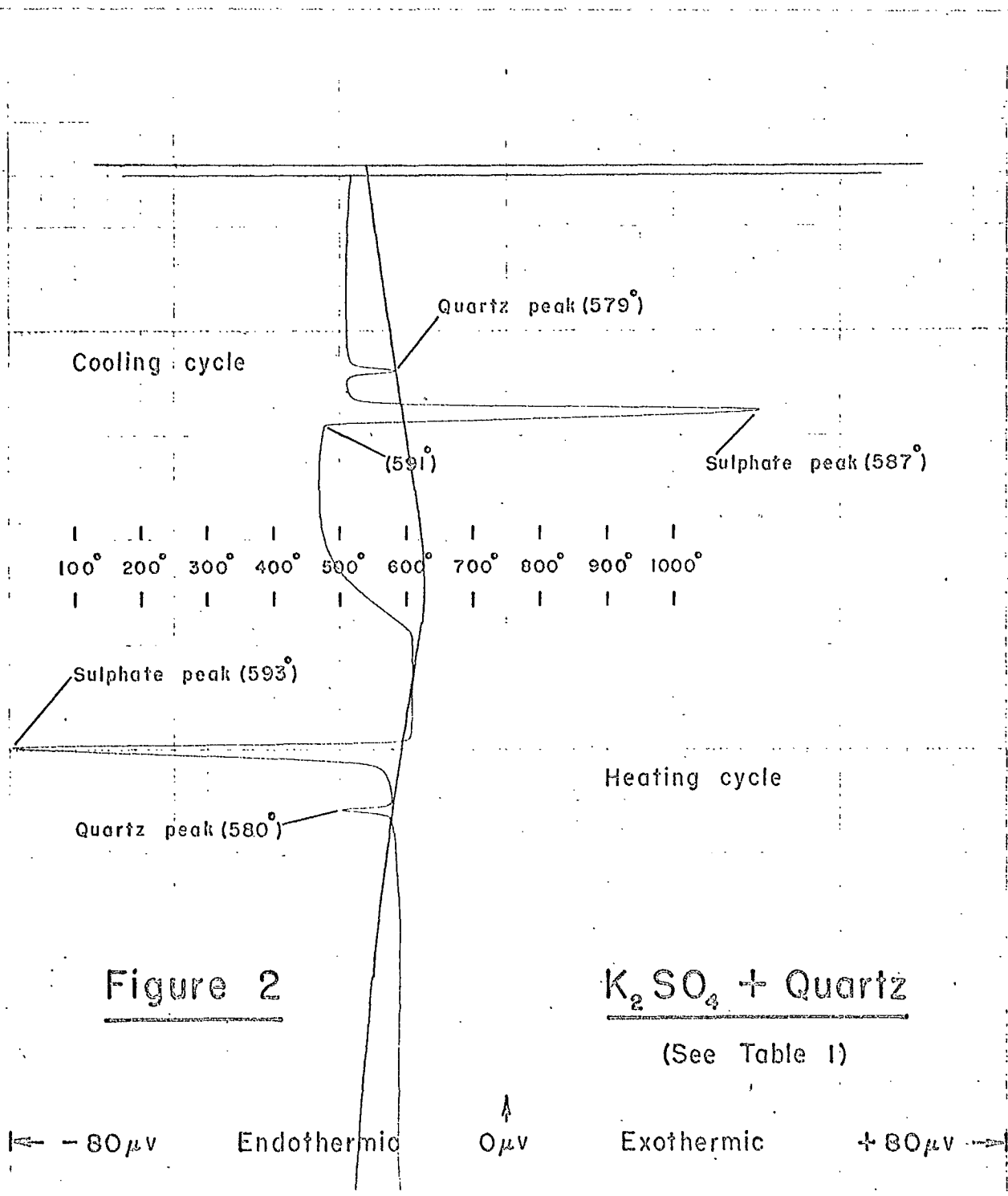


FIGURE 3

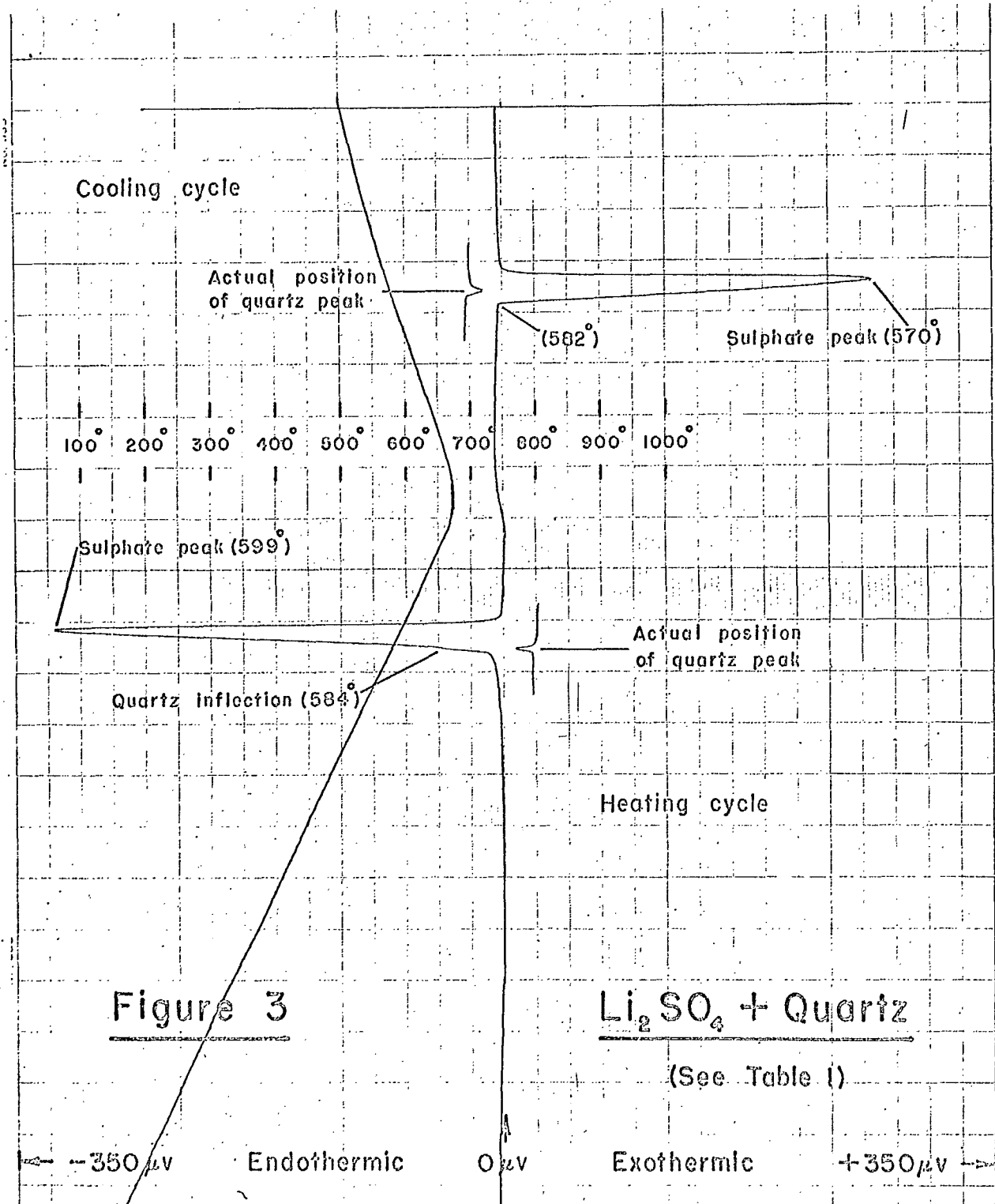


FIGURE 4

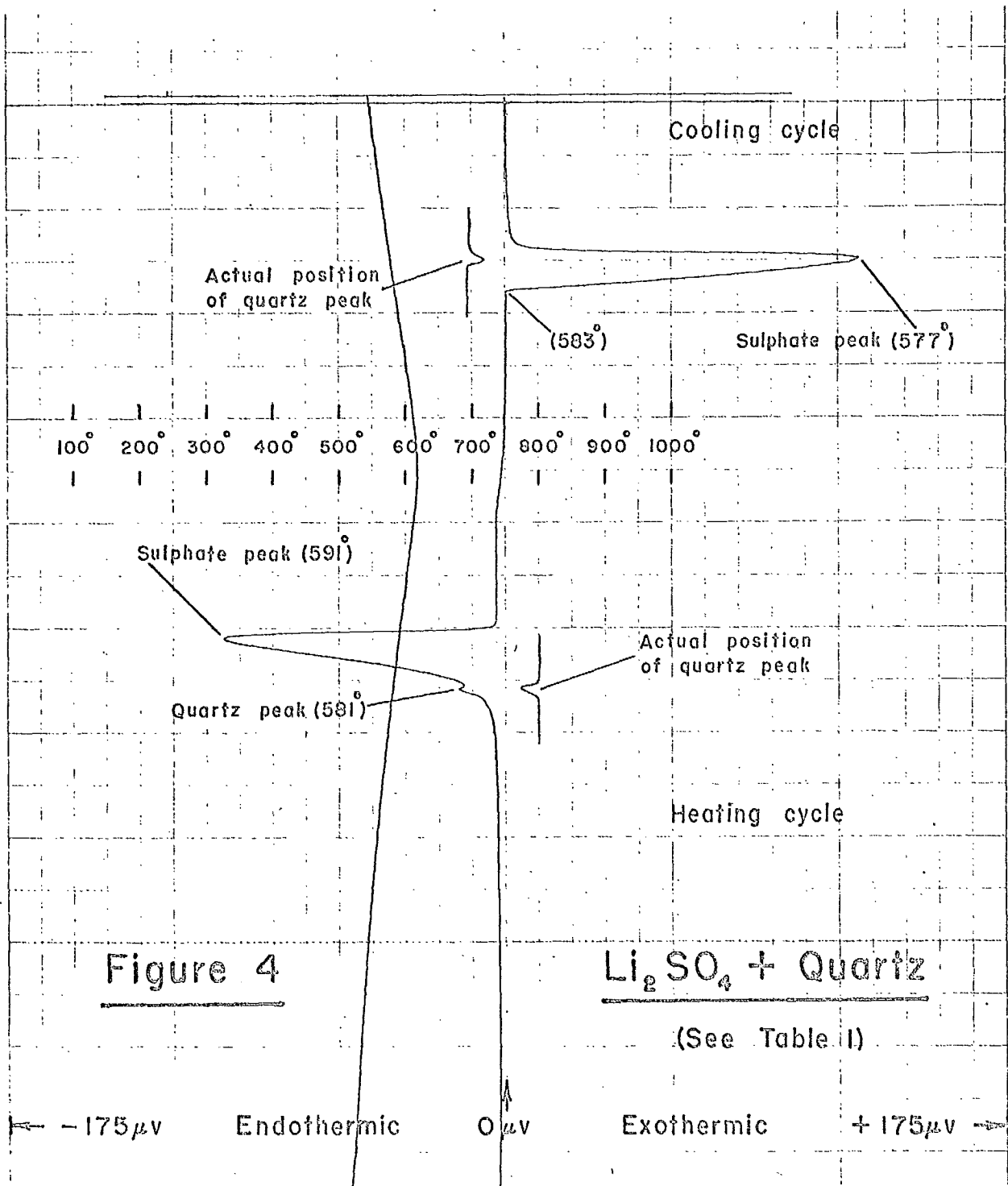


Figure 4



(See Table I)

APPENDIX

A complication that developed during the course of the investigation described in the body of this report concerned the appearance of a third, small, endothermic peak near the quartz inversion peak. This extra peak was smaller than the quartz peak and, on the thermograms of the K_2SO_4 - quartz mix, it appeared between the quartz and sulphate peaks, while, on the thermograms of the Li_2SO_4 - quartz mix, it appeared 5 to 10 deg C lower than the quartz peak. This extra peak was always accompanied by another very small peak at about 440°C and both were reversible on the cooling cycles of the tests. Figures 5 and 6 are photographic reproductions, reduced in size, of thermograms of both mixtures, run at the 3-degree/minute heating and cooling schedule, which show the extra peak near the quartz endotherm but not the very small extra peak at about 440°C because of space limitations.

To investigate the cause of these extra peaks, a series of tests was made in which 100-mg samples of K_2SO_4 and of Li_2SO_4 were substituted for their molar mixtures with quartz. It was observed that the extra peaks usually did not appear on the heating cycle of the first run but did appear on the cooling cycle and, thereafter, on both heating and cooling cycles of subsequent runs on the same sample. Figures 7 and 8 are photographic reproductions, reduced in size, of thermograms which show the extra peaks on the DTA curves of K_2SO_4 and Li_2SO_4 that were run at the 3-degree/minute schedule.

The possibility of thermocouple contamination was considered first, but was eliminated as the cause when tests showed that the extra peaks persisted on the thermogram of a given sample whether platinum/rhodium-alloy difference couples or chromel/alumel couples were used, even when they were newly re-beaded. This pointed to the samples as the source of the extraneous peaks either from impurities present in the samples, as received,

or by contamination from the sample holder. Semi-quantitative spectrochemical analysis of the samples, as received, revealed no significant impurities and, therefore, the sample holder became suspect.

The metal sample holders used in the DTA apparatus are periodically cleaned with molten Na_2CO_3 and then leached in dilute HCl , especially if they have become discoloured after a series of runs or if they have become obviously contaminated by a sample that had been vitrified and difficult to remove. However, it is usually sufficient, at the completion of a DTA run, to remove the sample and scrape or brush away any particles that may cling to the walls of the sample cavity, and then to blow out any remaining dust or particles with a stream of compressed air, and, in this series of tests, as far as visual inspection could determine, this was all that was required.

It was subsequently shown, however, that this procedure was inadequate for, when samples of K_2SO_4 and Li_2SO_4 were submitted to semi-quantitative spectrochemical analysis after having been cycled through their crystal inversions several times in the palladium sample holder, it was revealed that they contained palladium as an impurity. Similarly, samples of K_2SO_4 and Li_2SO_4 that were given the same heat treatment in a platinum/rhodium-alloy sample holder were found to contain platinum as an impurity. The presence of barium as a significant impurity was also detected in a sample of K_2SO_4 that had been heated in a palladium sample holder that had previously been used for tests with BaCO_3 . It thus became clear that, even at the relatively low temperatures used in these tests, the sulphates and carbonates of the caustic alkalies and alkaline earths may react with, and/or be absorbed by, sample holders made from noble metals such as palladium or platinum and, as impurities, may then enter into and react with the next sample tested in the holder. By running tests on K_2SO_4 containing 0.5% of Li_2SO_4 as an impurity and on Li_2SO_4 containing 0.5% K_2SO_4 , it was demonstrated that enough of the compound $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ was formed in each case to produce a small peak at about 440°C . Tests with

Li_2SO_4 which contained BaCO_3 as an impurity also showed that a compound was formed which registered a peak in the $550^\circ\text{-}560^\circ\text{C}$ temperature range.

Thus, apparently, the extraneous peaks were the result of very small amounts of impurities, from previous samples, held on or in the wall of the sample cavity of the holder (and also in the platinum foil discs) which, although not detectable by visual inspection, were enough to contaminate the sample. Once the sample holder was cleaned with molten Na_2CO_3 and leached in dilute HCl for each series of runs with a different mixture the extra peaks were eliminated.

Table 2

Conditions of Test for Thermograms

Figure	Figure 5	Figure 6	Figure 7	Figure 8
Sample	K_2SO_4 +quartz	Li_2SO_4 +quartz	K_2SO_4	Li_2SO_4
Sample weight	100 mg	100 mg	100 mg	100 mg
Heating rate	3 deg C/min	3 deg C/min	3 deg C/min	3 deg C/min
Cooling rate	3 deg C/min	3 deg C/min	3 deg C/min	3 deg C/min
Sensitivity*	15 μ v/inch	35 μ v/inch	15 μ v/inch	60 μ v/inch
Atmosphere	Static air	Static air	Static air	Static air

Difference couple - chromel vs alumel

Chart speed - 10 in./hr

Figures 5 to 8 follow on pages 16 to 19, respectively.

*Referred to original 10-in.-wide chart paper.

FIGURE 5

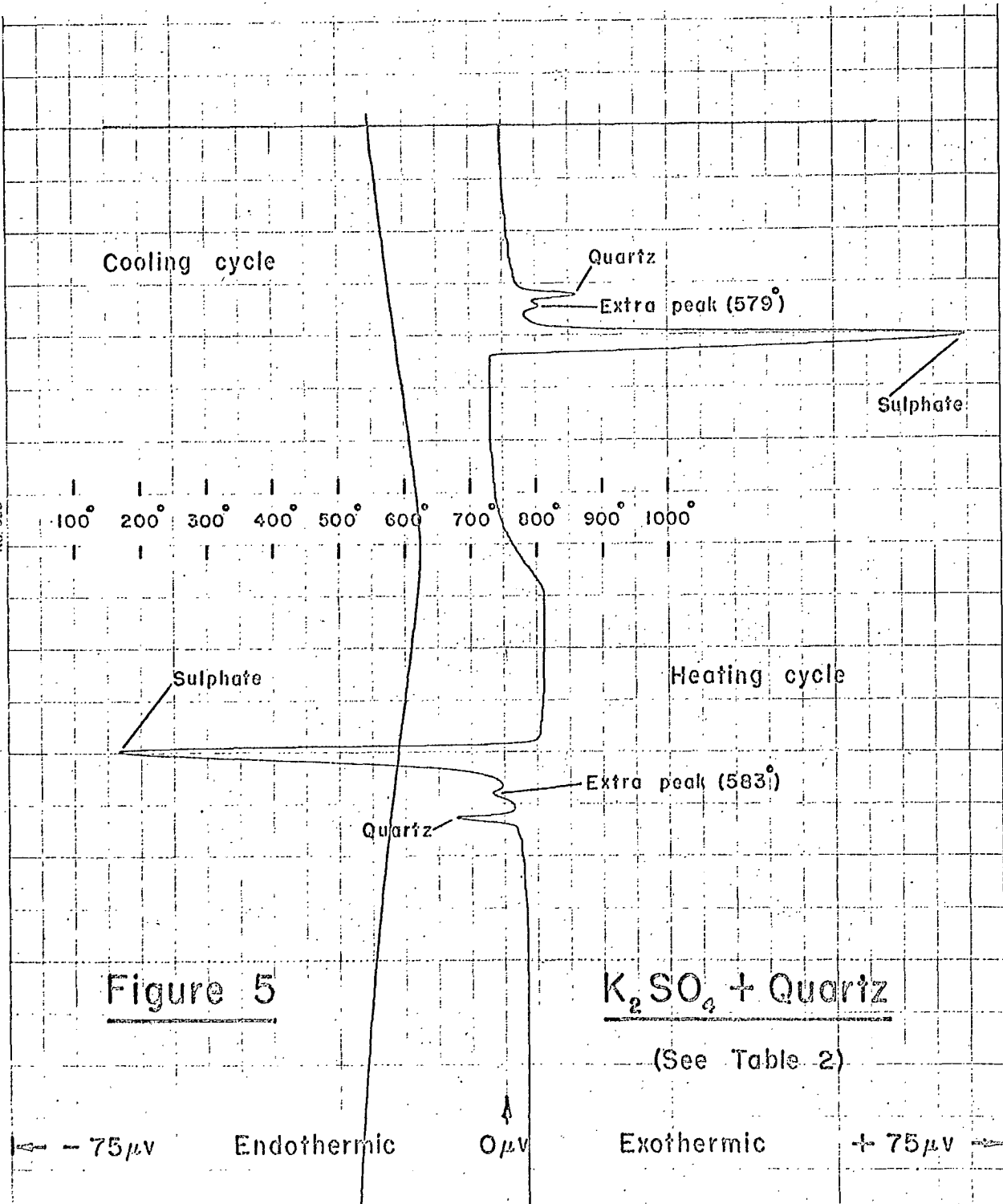
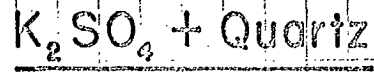


Figure 5



(See Table 2)

FIGURE 6

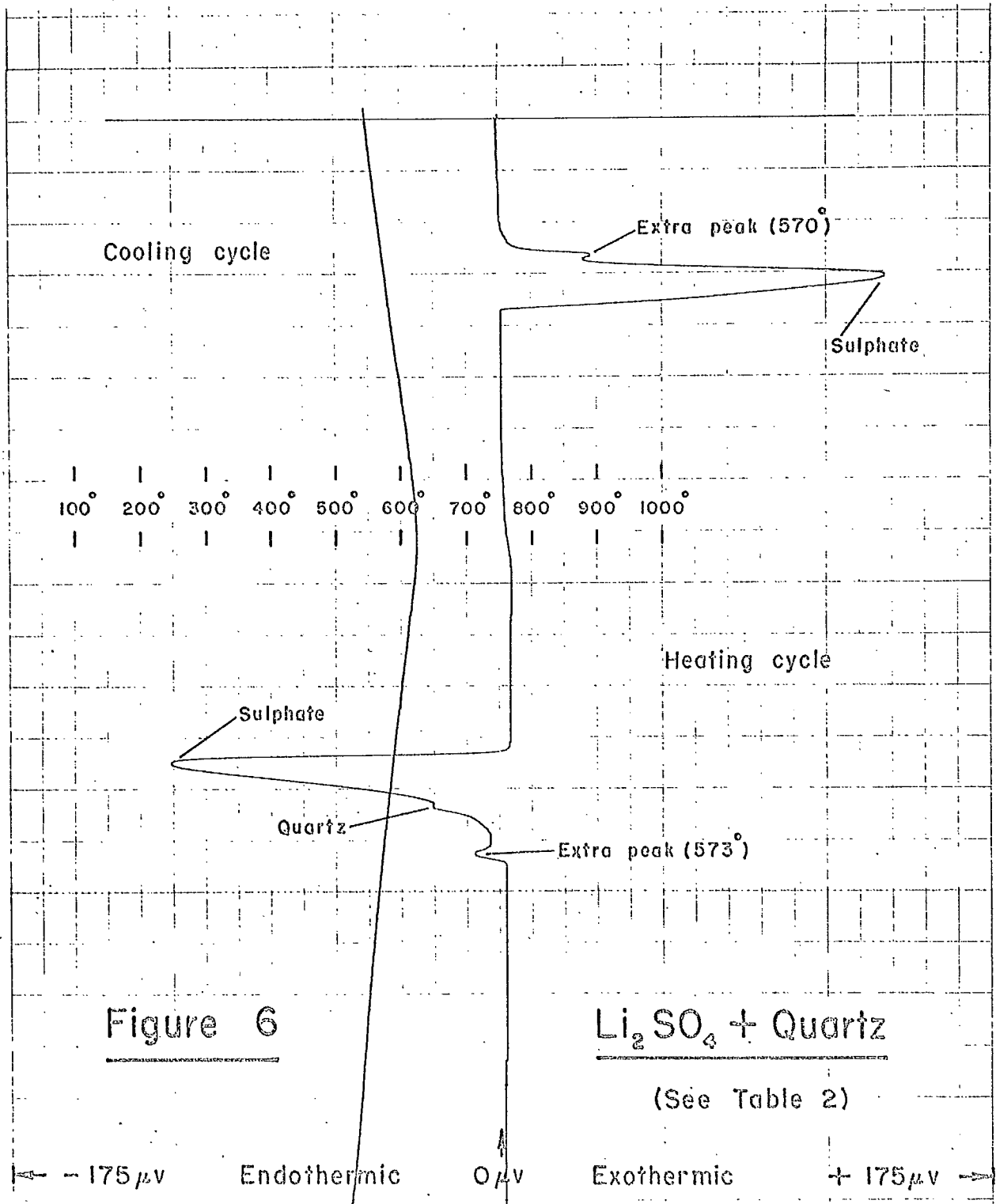


FIGURE 7

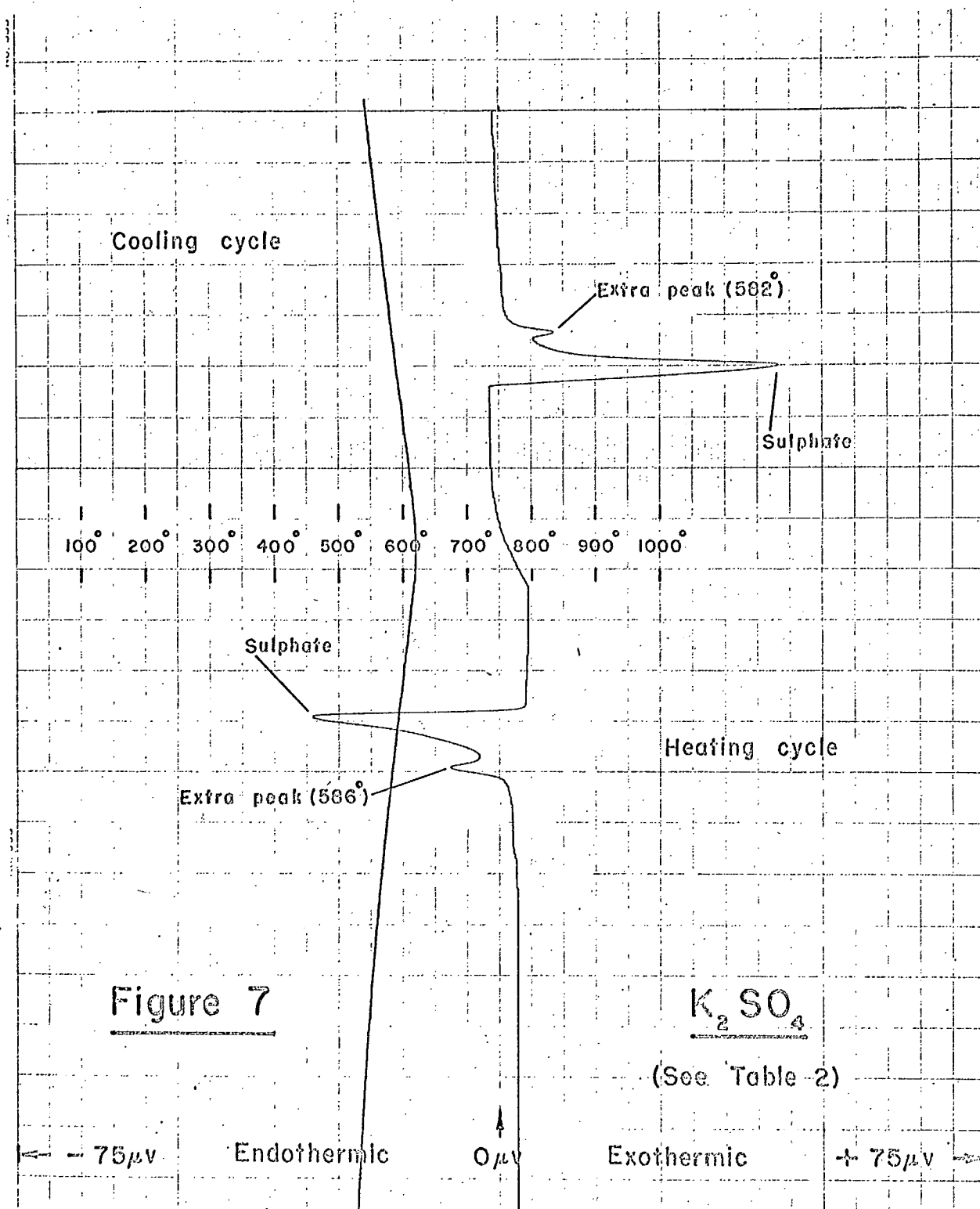
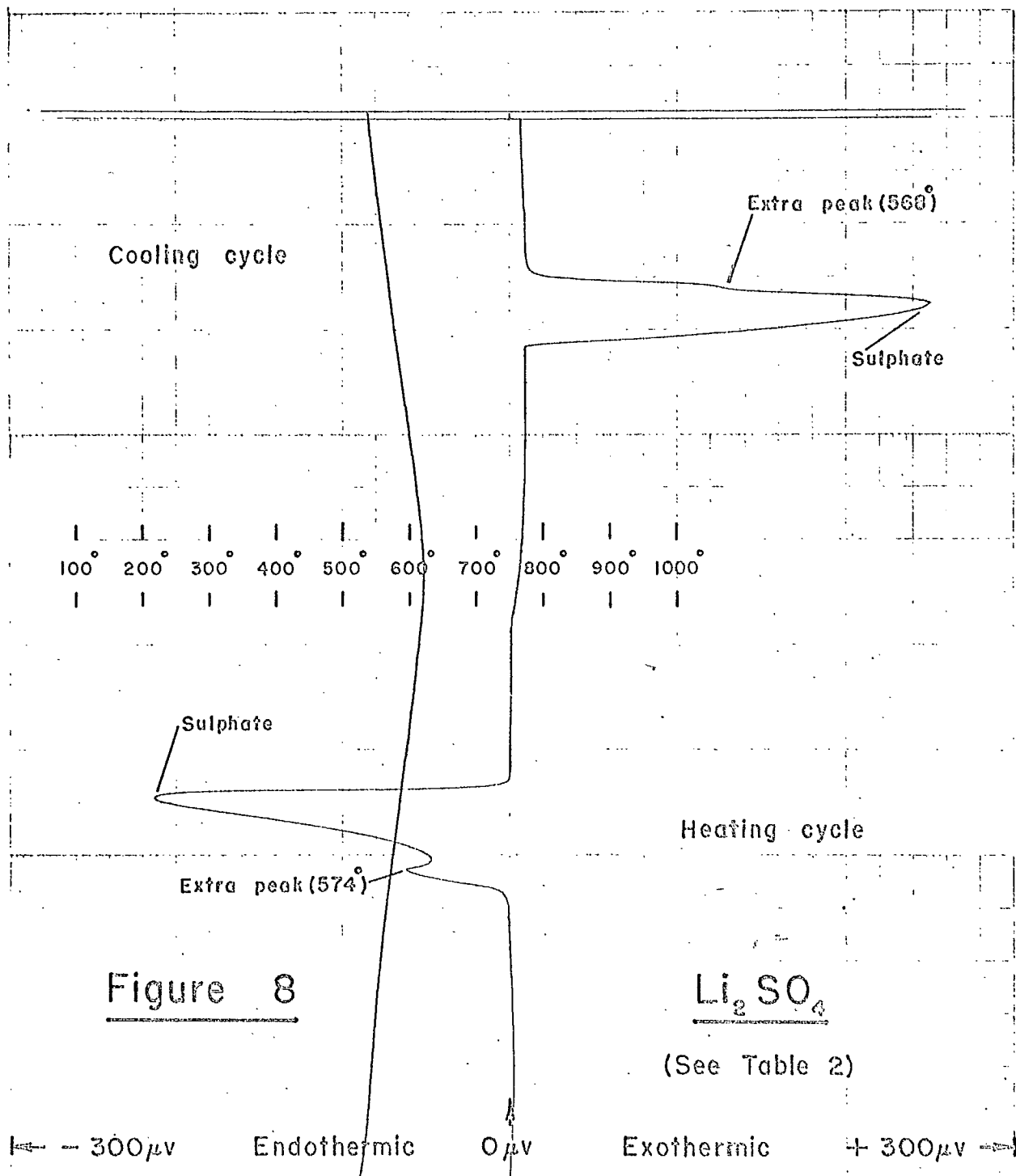


FIGURE 8



ACKNOWLEDGEMENT

Thanks are due to Mr. D. P. Palombo, Technician, of the Spectrochemistry Section, Mineral Sciences Division, for performing the semi-quantitative spectrochemical analyses on the several samples.

REFERENCE

1. Richard H. Lake, "The Construction, Operation and Performance of an Equipment for Differential Thermal Analysis", Mines Branch Technical Bulletin TB 92, August, 1967.