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MASS SPECTROMETER IN INVESTIGATION OF THE ANNEALING PROCESS OF THE THERMOLUMINESCENCE PHOSPHORE

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ÖZET

Termolüminesans radyasyon dozimetrelerinin yapılmasında kullanılan doğal calsiyum florürlerin yapım sırasında üzerlerine uygulanan anile (belli bir sıcaklıkta ısıtma) işleminde kimyasal değişmelerin olup olmadığını görmek için 2001 GC-MS Time of Flight kütle spektrometresinin kullanılması düşünülmüş ve bunun için bazı parçalar tasarlanarak sisteme ilave edilmiştir.

Doğal Ca F_2 (No: 18 blue) alınarak buna anile işlemi değişen sıcaklıkta uygulanmış ve sıcaklık 650°C olana kadar yavaş olarak ısıtılmıştır. Kütle spektrometresinde elde edilmiş olan spektrumlardan ısıtma işlemi sırasında fosforda bazı kimyasal değişmelerin olduğu gösterilmiş çıkan gazlar içerisinde su ve karbondioksidin varlığı belirtilerek diğer gazların belirlenmesi şimdilik yapılmamıştır.

ABSTRACT

Annealing process which is very important to obtain stable thermoluminescence character of the radiation dosimeters is investigated by using the Bendix 2001 GC-MS Time of Flight (T.O.F.) mass spectrometer. Natural calcium fluorite (No: 18, blue) is subjected to the annealing process in the range of 650°C and the evolved gases are recorded by mass spectrometer instantaneously. (m/e), 12, 15, 16, 17, 18, 20, 22, 24, 25, 26, 27, 28, 39, 40, 41, 42, 43, 44 peaks are detected. This experiment has not performed to analyse the evolved gases and resudues in the sample. But instead to show a way how this can be done using a mass spectrometer.

INTRODUCTION

Thermoluminescence dosimeter which is useful to measure exposed radiation doses of gamma or x-rays in a very wide range of doses from the few milirontgens to 10^5 rontgen. The stability and reproducibility of the phosphor depends on the previous processes effective to have better thermoluminescence character. Since it is not completely known that what happens to the sample during the annealing process spe-

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cially for the first time when preparation operation continues to have thermoluminescence radiation dosimeter.

Performing the annealing process next to the mass spectrometer is going to help to explain the process in chemical view.

INSTRUMENTATION

Bendix 2001 GC-MS (T.O.F.) mass spectrometer used together with some designed units connected to the mass spectrometer by modifying the inlet systems of the instrument. Modifications and units will be described separately in detail.

1. Specifications of 2001 GC-MS (T.O.F.) Mass Spectrometer

This instrument is the combination of a Bendix MA-2 mass spectrometer with a Bendix series 2600 gas chromotograph. It has three different inlet systems in production.

i) Gas and volatile liquid inlet system

This system can be connected to the mass spectrometer via an adjustable capillary tap. This unit has a separate mechanical pump to evacuate the system as about 10^{-3} torr.before the sample gas or volatile liquid vapor released into the inlet system. The sample gas should be stored in a large (approximately 5 litres) reservoir present in the inlet system. As soon as the gas pressure in the inlet system is at sufficient value the gas will pass through into the ionization source of the mass spectrometer via the opened capillary tap as a result of pressure difference between the inlet system and the mass spectrometer in which the pressure is maintained as about 10^{-7} torr by a oil diffusion pump.

ii) Gas chromotograph inlet system

Bendix 2600 gas chromotograph connected to the mass spectrometer via an interface for analysing the liquid samples.

iii) Solid Sample Inlet System

2001 GC-MS instrument has a direct insertion probe, which is made of quartz glass and is approximately 2.2 cm in diameter and 20 cm in length. This is passed through a vacuum locak and enables specimens to be introduced into close proximity to the ion source. The sample is volatilized by a small heating filament, and the temperature measured with an iron-constantan thermocouple, the output of which is shown on a digital display. The upper limit of the temperature is 400°C and maximum 10 miligram sample is acceptable.

For the vacuum, three Welch rotary pumps are in operation one for the gas inlet system and other for both the initial vacuum of the instrument so that the diffusion pump can able to operate for further vacuum and to exhaust the diffusion pump continiously during its operation. The third Welch pump operates for both gas chromotograph and solid inlet system. High vacuum can be obtained by the use of the CVC oil diffusion pump with a pumping speed of 760 Lt/sec. It also has a freon cooled baffle between the flight tube and the diffusion pump.

The instrument has an electron impact ion source, with 0-100 eV electron energy, providing 2.7 kV ion energy to the analysing unit which is field free region in length of one meter, next to the source With this unit the resolution of T.O.F. mass spectrometer being about 300-400 amu for organics and 500-800 amu for inorganics.

The relatively long flight path of the instrument would permit some spreading of the ion beam slight miss alignment of the ion trajectory would cause large losses in ions reaching the cathode. To correct trajectory errors, pairs of horizontal and vertical deflection plates operating at potentials about the ion energy potential are incorparated in the flight tube, and adjustment of the standing potentials applied to these plates will permit maximization of the ion current.

Ion detection is achieved by the use of a magnetic electron multiplier. Which permits three different outputs that one is the oscilloscope output which can be used as total output for the ions in the selected mass range. The gains of from 10^5 to 10^9 were obtainable.

2. Annealing Unit

This is shown schematically in Figure-1. The sample holder was located in a small filament furnace

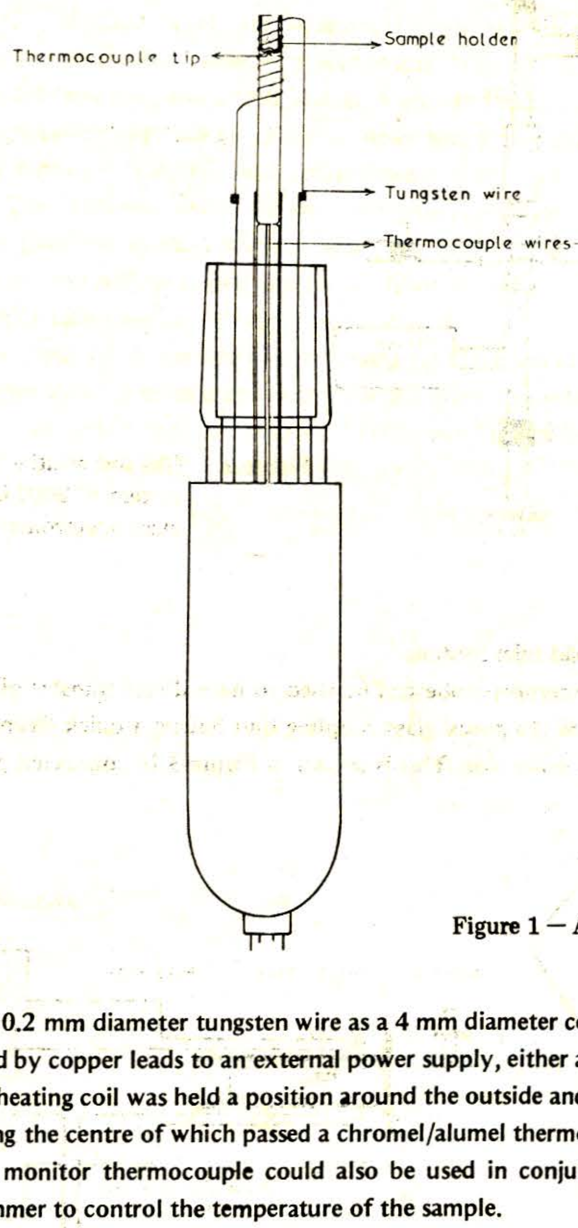

Figure 1 — Annealing unit

made by winding 0.2 mm diameter tungsten wire as a 4 mm diameter coil of 2 ohm resistance. This heating coil was connected by copper leads to an external power supply, either a variac or a temperature controller/ programmer. The heating coil was held a position around the outside and at the top of a close fitting central ceramic tube, along the centre of which passed a chromel/alumel thermocouple used to monitor the sample temperature. The monitor thermocouple could also be used in conjunction with a suitable temperature controller/programmer to control the temperature of the sample.

3. Coupling Units

To connect the annealing unit to the mass spectrometer the coupling units should be included by modifying the conventional inlet systems.

i) Modification On The Gas and Volatile Liquid Inlet System

As seen from the Figure-2, reservoir A combined with a suitable quick fit joint attached to the system to be able to connect the annealing unit. This unit also can be used by connecting to the fitting located to the reservoir B.

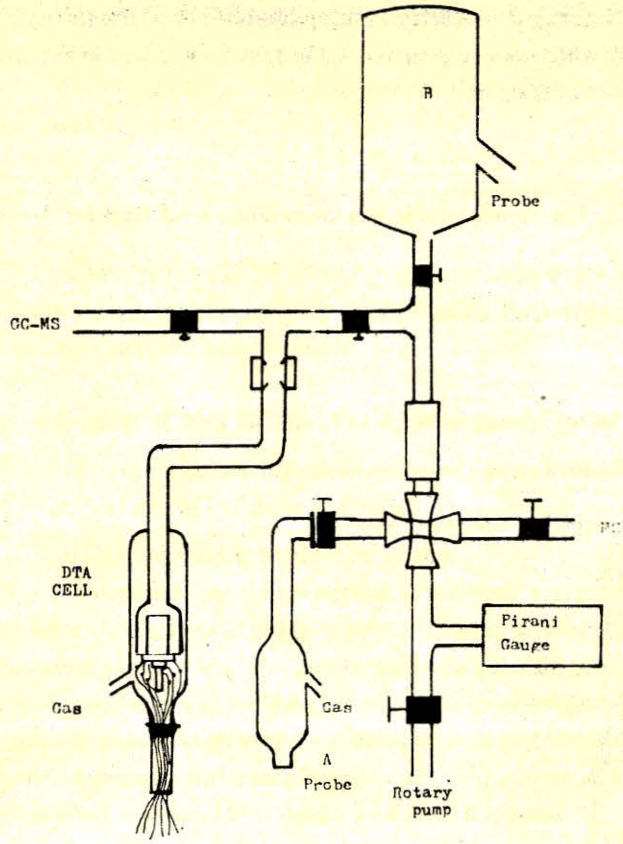

Figure 2 — Gas and volatile liquid inlet system of 2001 GC-MS TOF mass Spectrometer

ii) Modification On The Solid Inlet System

The housing of the solid insertion probe can be used to have direct transfer of the evolved gases into the mass spectrometer by using the pyrex glass coupling unit having a quick fitting on one side and vacuum sealed metallic part on the other side. This is shown in Figure-3 in connected position with mass

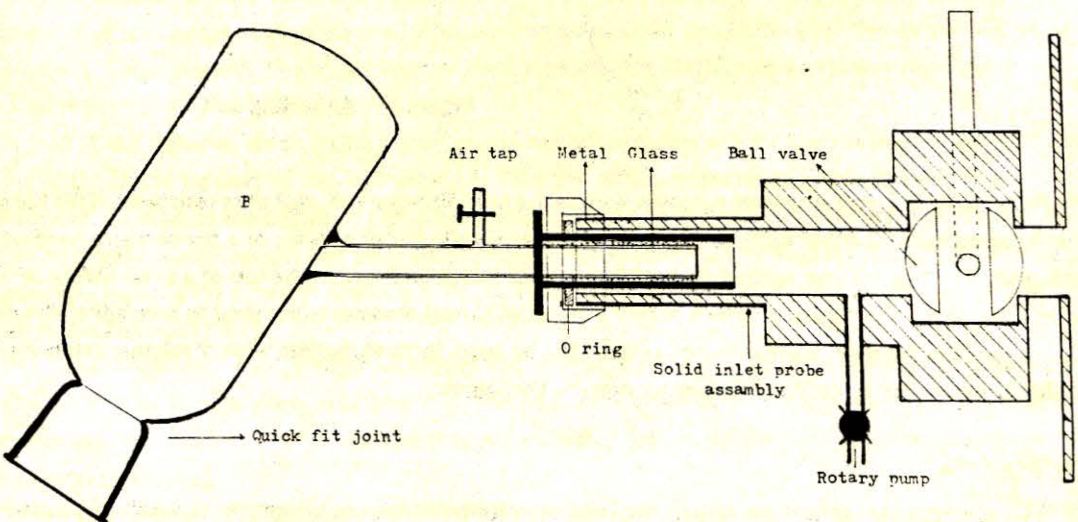

Figure 3 — Coupling unit for 2001 GC-MS TOF mass spectrometer

spectrometer. Because of the original solid inlet probe of the instrument has a sample capacity of maximum 10 miligrams and its temperature capacity can be increased up to maximum 400°C, this unit is designed and used with a large sample capacity as about 1 gr and with a temperature capacity of 700 C°.

EXPERIMENTAL RESULTS

In the early work[1,2] twenty different calcium fluorite sample collected from the different part of Turkey are investigated as thermoluminescence dosimeter material. Some of them were very sensitive and very stable in measuring the radiation doses of gamma and X-rays seperately. But before they have been used as dosimeter material, it should be applied annealing process in a long time to obtain stable character. So it is investigated in chemical way either is there any change or not in its structure. One of the calcium fluorite samples (no: 18, blue) is selected for annealing process using the system which is a part of designed units used to study decomposition kinetics of lead oxalate[3,4].

In operation, the coupling unit is placed as seen in Figure-3 and the unit described and shown in Figure-2 is fitted together with the sample in it. After the air tap closed rotary pump is operated to evacuate the volume separated from the mass spectrometer by the ball valve. When the ball valve is taken to the open position, the high vacuum of the mass spectrometer which is obtained by operating the diffusion pump, hava been governed in the system in which the sample is located. When the experiment has been complated, the ball valve will be closed and the air from the air tap will be driven into the system and the annealing unit can be taken out of the system to start again.

The back ground mass spektrum of the instrument is detected and then power supply is applied on the filament furnace by temperature controller/ programmer. The spectrum at 300 C° and 650 C° are obtained and shown in Figure-4 together with the back ground spectrum. By comparing this spectrums with

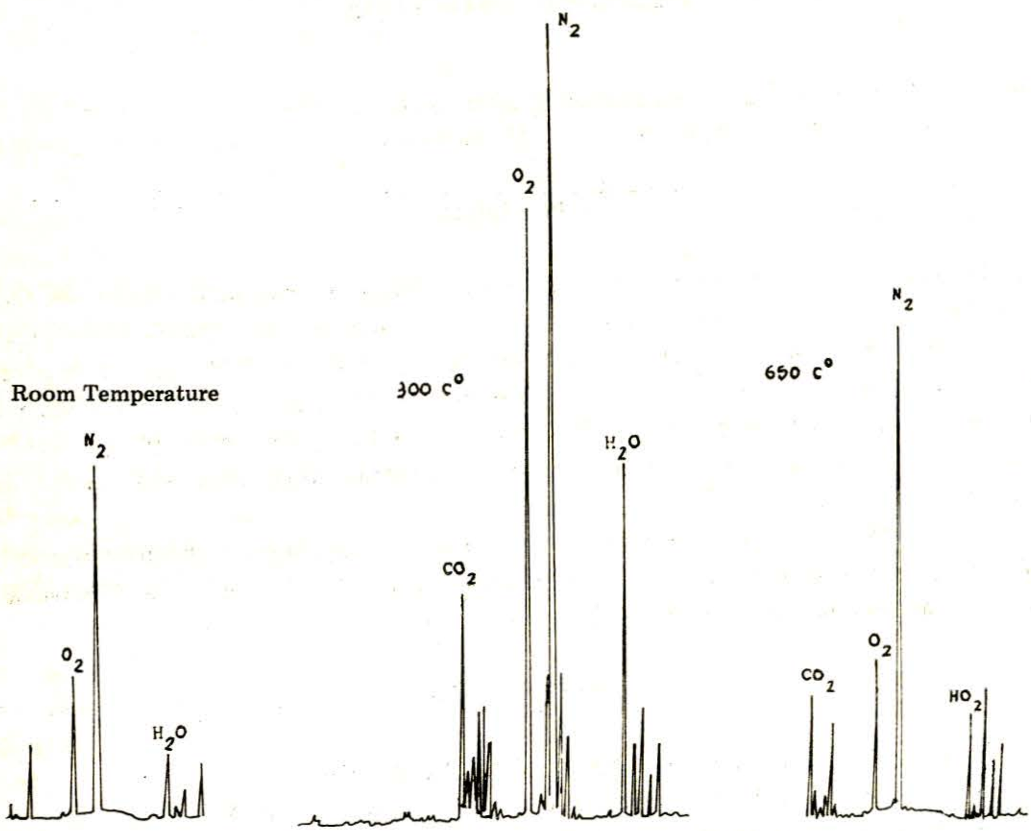

Figure 4 — Mass spectrum of the natural CaF_2 in the annealing process

the spectrum of pure CO_2 gas shown in Figure-5, it is possible to say CO_2 is present in the evolved gases produced at 300 C° and 650 C° in the annealing process. Other fragments in the mass spectrum have been

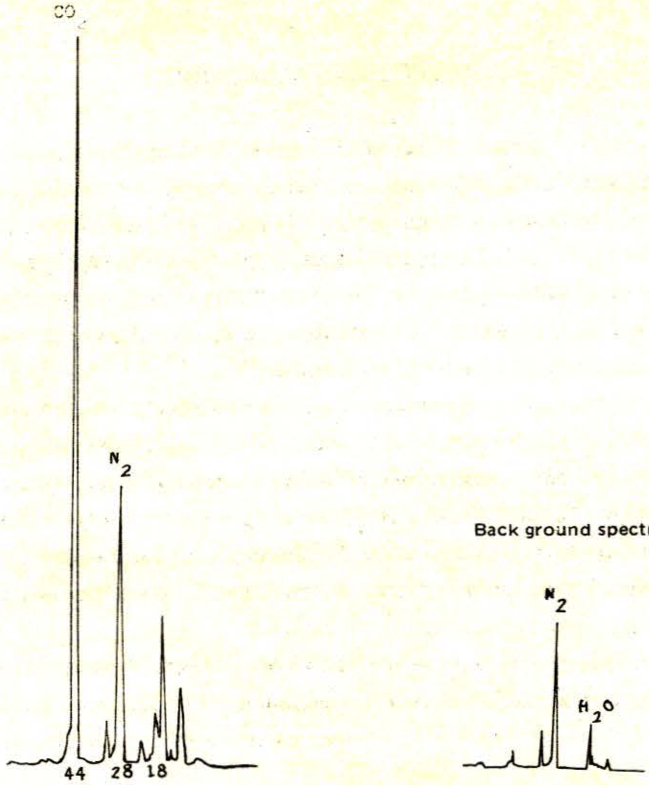

Figure 5 — Spectrum of CO_2 gas

idantified in the next work. But it is obvious that the peaks obtained from the spectrum are m/e: 12, 15, 16, 17, 18, 20, 22, 24, 25, 26, 27, 28, 39, 40, 41, 42, 43, 44. As known m/e = 17 and 18 are the water peaks.

DISCUSSION

The phosphore obtained from the natural sources contains organic and inorganic materials in it's structure. These impurities if present, decompose under the heating process producing evolved gases and residues in the structure of the phosphore. The product gases can be detected by the mass spectrometer and can be identified completely. The residues can also be analysed by mass spectrometer combined with high temperature solid inlet system. These residues stay in the solid structure of the phosphore as impurities which are the source of the electron traps that the thermoluminescence phenomenon can be explained by these traps.

The method mentioned in this work just to show how can be obtained full information about the annealing process products if any, by using the mass spectrometer. Including, to decide which temperature will be applied and how long the annealing process will be continued.

REFERENCES

1. Selçuk, A.; Technical Journal, A.N.A.E.M., Vol: 3, No: 2, 1976.
2. Selçuk, A.; Ph. D Thesis, U.Ü. Mühendislik Fakültesi, Balıkesir-TURKEY.
3. Selçuk, A. and Price, D.; Dynamic Mass Spectrometry 6, 126 (1981). "Development of Various Mass Spectrometric Thermal Analysis Techniques and Their Application to Study The Decomposition Kinetics of Lead Oxalate".
4. Selçuk, A.; "Further Development of Mass Spectrometric Thermal Analysis Technique", Unpublished Work.