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THERMAL ACTIVITIES IN GREECE*

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Abstract

The history of the Hellenic Society of Thermal Analysis (HSTA) is outlined. A review of thermal activities in Greece is presented, concentrating on polymeric and inorganic materials, minerals and pharmaceuticals. Some examples are given.

Keywords: HSTA, inorganic materials, minerals, pharmaceuticals, polymers

Introduction

In Greek mythology, it is told that Prometheus stole fire from the home of the Gods on Mount Olympus, and brought it to mankind. The use of fire to cook foods contributed to the welfare of early peoples, and cooking can perhaps be regarded as the very first 'chemical experiment'. During the sixth century B.C, observation and experiment were recommended by Greek philosophers as methods of scientific research. In particular, Platon introduced thermal analysis issues by defining the terms 'freezing' and 'melting' from his observations of the dehydration of heating tiles and his descriptions of materials that are not decomposed by fire, that is inert materials.

One and a half centuries later, another Greek philosopher, Theophrastos, applied the methodology of experiment and the usage of fire, and distinguished ores and minerals. At the same time, Straton succeeded in two experiments, first to dilute the air enclosed in a pot by elevating the temperature, and secondly to prove that coke (optanthrax), derived from stone-carbon by heating, has a lower mass than that of the original material, although it maintains the same volume.

It could be considered that these observations brought the first message of thermogravimetric and thermodilatometric analysis (TG and TDA), although only in the late 19th century did experiments on the effects of heat on materials become more controlled and more quantitative. With the development of commercially available instruments, suitable for measurements of parameters of sev-

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eral properties as a function of temperature, and the establishment of the ICTA (International Confederation for Thermal Analysis) in 1965, thermal analysis techniques have now become familiar worldwide.

In Greece, the need for communication and cooperation between people working in the field of thermal analysis resulted in the establishment of the Hellenic Society of Thermal Analysis (HSTA). Officially, HSTA was 'born' in 1995 in Athens and accepted as an affiliated society of ICTAC, although as an idea it was conceived several years previously. This national scientific organization is comprised of about 100 individual members from universities, research institutes and private or state laboratories and is administered via the statue by the HSTA Council consisting of an Executive Committee. This Committee organized the first national workshop in thermal analysis in Athens in April 1996 [1]. At this meeting, Greek scientists presented their work on several topics of applications and possibilities of thermal analysis of various types of materials, by using essentially the techniques of TMA, DMA, DTA, DSC and TG/DTG in combination with other complementary techniques such as mass spectroscopy and infrared spectroscopy. Since their work is widely scattered, as a direct consequence of the diversity of the instrumentation, methodology and applications relevant to these techniques, an attempt at classification is made here according to the main fields of application and the materials studied.

Selected topics

Polymeric materials

Preparation and characterization

The preparation of polymers, such as polyamides, polyurethanes, thermoplast polyesters, copolymers of polyethyleneoxides or N-vinyl-carboxylates, is achieved by well-established methods. Their characteristic thermal behaviour depends greatly on their nature, preparation and treatment. The products or intermediates of the reaction may be analysed by infrared spectroscopy (IR) and by thermogravimetric analysis (TG). For the characterization of polymers, very specific treatment is required, especially when the ASTM method is involved, in order to measure the glass transition temperature, T_g, melting point, T_m, and crystallization temperature, T_c, using the DSC technique [2].

The results obtained from DSC experiments have been correlated with those found from rheological measurements and from dynamic scattering of light and dielectric spectroscopic observations [3].

Cure

The glass transition temperature, T_g, for a thermosetting polymer is a property which depends on the conversion degree of the curing reaction. The initial T_g of the starting material is followed by the large exotherm of the polymerization reaction. The increase in the cross-linking density reduces the mobility of chain segments, and consequently T_g increases. Thermal analysis is a very useful tool for characterization of the physical properties of thermoplastic materials and finished products. When the thermosetting system is fully cured, T_g becomes a characteristic thermal property of the system, known as the maximum glass transition temperature. Its measurement is performed by DSC in the second scan, after a previous scan, by heating up the sample to a temperature at which the exothermic curing reaction is completed [4].

Sometimes, however, the end-temperature in the first scan may be enough to produce thermal degradation of the polymer. To avoid this, the T_g values are determined via isothermal curing at different temperatures and times of reaction. In order to understand the mechanism and kinetics of cure reactions, the first essential step in the process, is the measurement of ΔH (heat of the cure reaction) isothermally.

Liquid crystals

Liquid crystals comprise a most popular class of advanced materials in modern life. The advances extend to fields such as electro-optical displays, flat screen displays for computers and televisions and temperature-sensing devices. Liquid crystals or mesogenic compounds are materials which exhibit mesomorphism. Under certain conditions, the phases formed do not correspond to an ordered solid or to a disordered liquid, and are called mesophases. The three identified types of liquid crystalline phases are called smectic, nematic and cholestic phases.

There are two different ways of taking a crystal to a mesophase.

a) by heating the crystalline solid or cooling the isotropic liquid (thermotropic liquid crystal) or

b) by dissolving the compound in a suitable solvent under given concentration and temperature conditions (lyotropic liquid crystal).

The thermotropic materials are usually covalent, whereas the lyotropic ones are ionic. New compounds are synthesized and tested for liquid crystalline properties. The mesophase characterization of new materials is achieved

a) by combined methods, such as thermogravimetric, thermomechanical and dynamic thermomechanical analysis (TG, TMA and DMA),

b) by miscibility tests,

c) by calorimetric methods (DSC) for the determination of thermodynamic variables involved in phase transitions and

d) hot-stage polarizing microscopy (HSPM) for determination of the different textures at certain temperatures, where the transitions occur.

Miscibility

The heat of mixing in liquids or compressed gases and the heat of adsorption in solids are evaluated by flow calorimetry. There are two main arrangements for these measurements:

i) a flow calorimetric device with a fast temperature response, suitable for running experiments at high pressure, and

ii) a flow calorimetric device under low pressure for the measurements of adsorption in solids.

Miscibility studies on polymers also involve conventional thermal analysis by using TG and DSC techniques. The available differential scanning calorimeter has the ability of fast cooling (fast quenching DSC) and can attain –190°C.

The available spectrometer, FTIR, connected with the TG system, permits the identification of thermal decomposition products of polymers. Alternatively, with a special modification, the IR spectra may be measured at various temperatures as the sample is heated in a thermally controlled IR cell. This technique gives valuable results in the study of liquids, polymeric membranes and supercritical gases. Recent applications include miscibility studies on polymers, the kinetic estimation of parameters of polymerization reactions, control of the oxidative stability of polymers, control of sol–gel processes and studies of changes in the transition phase of a polymeric matrix [5–7].

Thermomicroscopy

In thermomicroscopy, an optical property of a sample, monitored *vs.* time or programmed temperature, is observed under a microscope [8]. Liquid crystals and solids will convert light into polarized light due to differences in refractive index in the different directions, and produce colours characteristic of the sample. At a phase transition temperature, a change in polarization will occur. The colours observed and the light intensity also change at the transition. The available thermomicroscope permits the study of equilibrium phases of polymers with the sample under the optical microscope. Since the cloud change (scattering of light) is observed at the point of phase separation in complex systems, thermomicroscopy is used for the determination of cloud curves in polymeric mixtures. With the use of a polarized thermomicroscope, the crystallization of polymers and the appearance of the mesophases in liquid crystalline systems can be detected (cf. section Liquid crystals).

Plastics in contact with food

If samples of food materials cannot be kept under 'ideal conditions', they may deteriorate by adsorption or loss of water, or by altering the texture and appearance of the product. The loss of moisture may be studied by TG, while the small changes in thermal and mechanical properties can be followed by means of DSC and DMA, respectively.

Inorganic materials

The valuable applications of superconductors in motors and generators have led to efforts to produce new types of materials. The high-temperature superconductors, containing among others and one rare earth element, are produced by conventional (e.g. sol–gel and microwave) or new (CVD, chemical vapour deposition) technological methods, while their structural changes are followed by TG and DTA techniques.

The preparation and characterization (surface area, pore size distribution, acidity and catalytic activity) of the following classes of inorganic materials have been undertaken: mesomorphous alumina and alumina–aluminophosphates (AAP) (pure or modified with other components, such as Fe^{2+}, Ni^{3+}, V^{5+}, Ce^{4+}, etc), pillared clays and perovskites [9, 10]. For the preparation of these materials, the precursors are obtained by precipitation for alumina and AAP by impregnation for pillared clay and from dried solutions for perovskites. In all cases, thermal analysis is used to check the route of the removal and/or the decomposition of organic or inorganic components from the inorganic matrices during the heating of the precursors. The routes of these decomposition seem to affect the textural properties of the final solids for the AAP materials.

Study of reactions during sintering of mixed oxides, e.g. V_2O_5/Nb_2O_5, Zr_2O_2/Y_2O_3

On the basis of the allotropic forms that some metals exhibit (changes in their molecular structure) DSC investigations are made for their qualitative control during the production process.

Elastic behaviour

The mechanical properties of materials provide an essential guide to their suitability for some particular usage, and can indicate how the material has been treated before testing. The molecular nature of the material is most important in determining the mechanical properties. With the methods of TMA, DMA and DSC, the mechanical moduli in construction materials are studied systematically. Investigation of their elastic behaviour includes determination of the deformation types (tensile, shear or three-point bending). For materials with tensile modulus, the storage modulus E' and the loss modulus E' are determined, together with the loss tangent $\tan\delta = E'/E''$ [11].

Coordination compounds

The molecular structure of novel coordination compounds is based on physicochemical measurements such as elemental analysis, conductivity and magnetic susceptibility measurements and spectroscopic data {IR, electronic transitions in the UV-visible region, electronic paramagnetic resonance (EPR) and NMR spectra}. The structure is confirmed by single-crystal X-ray diffraction study. Knowledge of the structural features and the parameters influencing bond formation and chelate stability helps in the design of ligands with predetermined properties. Their redox properties, their thermal behaviour and their possible bioactivity are further examined.

The techniques used for the determination of thermal decomposition modes of coordination compounds in the solid state, are mostly simultaneous TG/DTG and DTA. Their thermal stability, their thermal decomposition, the intermediates and the residues at certain temperatures are examined in air and/or nitrogen atmosphere. The effects of the metal and the ligand on the reaction enthalpies are measured. The important factors are the loss of the ligand, phase changes and decomposition of the sample and of the products. In consequence of these complicated reactions and in order to obtain reliable results, complementary methods are used, such as pyrolysis with isolation and identification of the volatile products and IR and MS spectroscopy. Although the conditions in the ionic chamber are more drastic in mass spectroscopy, the fragmentation pattern and hence the decomposition mode are similar to those observed in thermogravimetry. The quasi-isothermal analysis (QIA) method has been used for determination of the mechanism of decomposition reactions. Kinetic parameter estimation (apparent activation energy E^*, reaction order n, frequency or pre-exponential factor Z, and rate constant k) for the main decomposition stage is also undertaken. The compounds studied include mainly the transition metals Cu, Ni, Co, Fe, Mn and Zn, and also Rh, Pd, Cd, As, Sb and Bi. The ligands used are dithiocarbamates, monohalogenbenzoylhydrazines, dichlorobenzoylhydrazines, hydroxyquinones, phosphoramides, sulfonylurea, thiones, phosphines and 2-hydroxyaryloximes [12, 13].

Composite materials

The following areas of research activities are covered: thermal analysis, mechanical identification and testing, environmental degradation, interfacial phenomena, adhesion between phases, modelling of polymeric composites, finite element and boundary element methods, design of sandwich structures, thermal stability, damage tolerance of composite structures, micromechanics, fracture mechanics and viscoelastic behaviour. In all the above areas, thermal analysis plays a major role as both an experimental key and a research area itself. TMA, DSC and DMA techniques are applied mainly to characterize new polymer-based composites such as fibre-reinforced and particulate-reinforced polymers [14, 15].

Cements

Cement, as a component of concrete, is used in building construction, roads, etc. It is made by heating clays, which are aluminosilicates, with calcium carbonate and consists chiefly of mixed calcium silicates. During the hardening process with water, the cement material slowly develops its final strength. The two main types of cement are Ordinary Portlant Cement (OPC), mentioned above, which on DTA gives a characteristic endotherm due to dehydration of $Ca(OH)_2$, and high alumina cement (HAC). The latter is made from bauxite and limestone and is mostly a mixture of calcium aluminates. These react with water and gain strength more rapidly than OPC and hence speed up the building process. The DTA profile curve of HAC is quite different from that of OPC. The cementing action of the silicate or aluminate hydrates is as much a physical as a chemical effect. Chemical bonds give coherence to the hydrate crystallites, but the crystallites themselves mechanically lock together, giving strength through the whole bulk of the cement. Due to chemical changes in the HAC (conversion of calcium aluminate decahydrate, $CaO \cdot Al_2O_3 \cdot 10H_2O$, to calcium aluminate hexahydrate, $3CaO \cdot Al_2O_3 \cdot 6H_2O$, or to gippsite, $Al_2O_3 \cdot 3H_2O$), it loses strength largely through the creation of pores. The conversion reaction is brought about by high ambient temperatures and is accelerated by moist conditions. Conversion may occur at the time of hardening, due to the heat of reaction, or after hardening, through inadvertent heating. The deterioration of cement in buildings (mainly in roof beams) can lead them to collapse catastrophically. DTA has proved valuable in assessing the degree of conversion (by measuring the volatile hydrates in cements) and hence the deterioration of concrete.

In Greece, the cement industry is one of the major consumers of both thermal and electrical energy. There are two companies, having at least three factories, which deal with the production of different types of cement: Titan and Iraklis (Herculus). The history of the Titan cement company coincides with the history of the cement industry. The company was founded at the beginning of this century, with a very small capacity, and it has now been developped into one of the best-known cement manufacturers worldwide. The quick switch from an oil fuel-burning process to solid fuel just after the shock of the second oil crisis helped the company to strengthen its position in highly demanding markets like those of the USA and Europe [16].

The initial cement composition varies with the raw materials, which consistently contain small amounts of minerals, such as compounds of Mg, Fe or Ti. The cements are examined for their raw materials, for quality control of H_2O, CO_2, kaolin, gypsum, solid fuels, limestone and metals, and for quantity control of $Ca(OH)_2$ and free CaO. During the cementing process, the rates of hydration of commercial cements and of the new ones prepared in scientific laboratories are followed, as is the relationship with their development in strength. Investigations of concrete deterioration in buildings are also undertaken in some laboratories. During the conversion process, the formation of pores reduces the strength of the concrete; accordingly, attempts to plan systems for the safe isolation of radioactive residues by studying the physicochemical state of water in the pores of cement are undertaken in the Demokritos scientific institute, which deals with radioisotopes.

The DSC technique has proved very useful in thermal profile studies during the clinkerization process, by burning farine, a mixture of grinding raw materials (clays, limestone and gypsum). The raw mixture is progressively heated to about 1450°C in a rotary furnace, so that partial fusion occurs, followed by rapid cooling of the product, termed clinker. For the design and operation of a mineral pyroprocessing system, DTA provides a direct method for the essential knowledge of the practical heat requirement needed to bring the feed material to its burning temperature [17].

Minerals

An attempt is made here at mineral classification based on chemical composition and internal structure. Bauxite, an earthy rock, occurs over a large area in central Greece; it contains a mixture of hydrous aluminium oxides in varying proportions. It is valuable as a source of aluminium. Its properties are examined by TG, DTG, TG and DTD (thermodilatometry and dynamic thermodilatometry) techniques. Due to its low density and great strength, aluminium has been applied for many uses, such as sheets and tubes in automobiles and airplanes where light weight is desirable. Aluminium is replacing copper to some extent in electrical transmission lines.

Study of the effects of metal oxides on the structures and physicochemical properties of calcium–aluminium–silicate compounds, and on their formation energies.

The potential beneficiation of low-grade Greek raw phosphate ores (located at Ipiros, North-West Greece) by conventional and innovational techniques, such as acid-thermal treatment and mechanochemistry is examined. An important step in the acid-thermal treatment of phosphate raw materials is the condensation of the intermediate acidic salts. The thermal polycondensation of the systems $Ca(H_2PO_4)_2 \cdot H_2O$–$CaHPO_4 \cdot 2H_2O$ and $Ca(H_2PO_4)_2 \cdot H_2O$–Si_2O [18] (where the raw phosphate materials contain silicate gangue) has been studied by thermal analysis.

Thermal analysis has been used as a useful tool for study of the mechanical activation of calcareous phosphate raw materials. Mechanical activation influences the thermal decomposition of calcite and francolite and their raw mixtures. The determined thermodynamic and kinetic parameters are changed by grinding in a planetary mill. The experimental design was a useful means of selecting the predominant mechanism of the solid decomposition under these conditions [19].

Thermal processes of carbon materials

The lignites from the Ptolemais Basin, Northern Greece, are under intensive exploitation by open-cast mining. The exploited lignites are used for electric power generation. In particular, fourteen steam electric stations are installed in the area of Ptolemais, producing 70% of the total electrical energy of Greece (Fig. 1). Mineralogical and chemical investigations on lignite and fly ash samples have been performed by several authors. The maceral composition and the reflectance of the individual macerals have been determined. Proximate analysis (water, ash, volatile matter and fixed carbon) and determination of elementary composition and oxygen functional groups are also performed [20].

The results of petrographic investigations point to the different compositions of the three maceral groups huminite, liptinite and inertinite and the inorganic minerals. The relationship between the petrographic and chemical composition and the TG/DTA data is usually examined. It has been concluded that the degree of initial biomass gelatification is followed by the same degree of coalification.

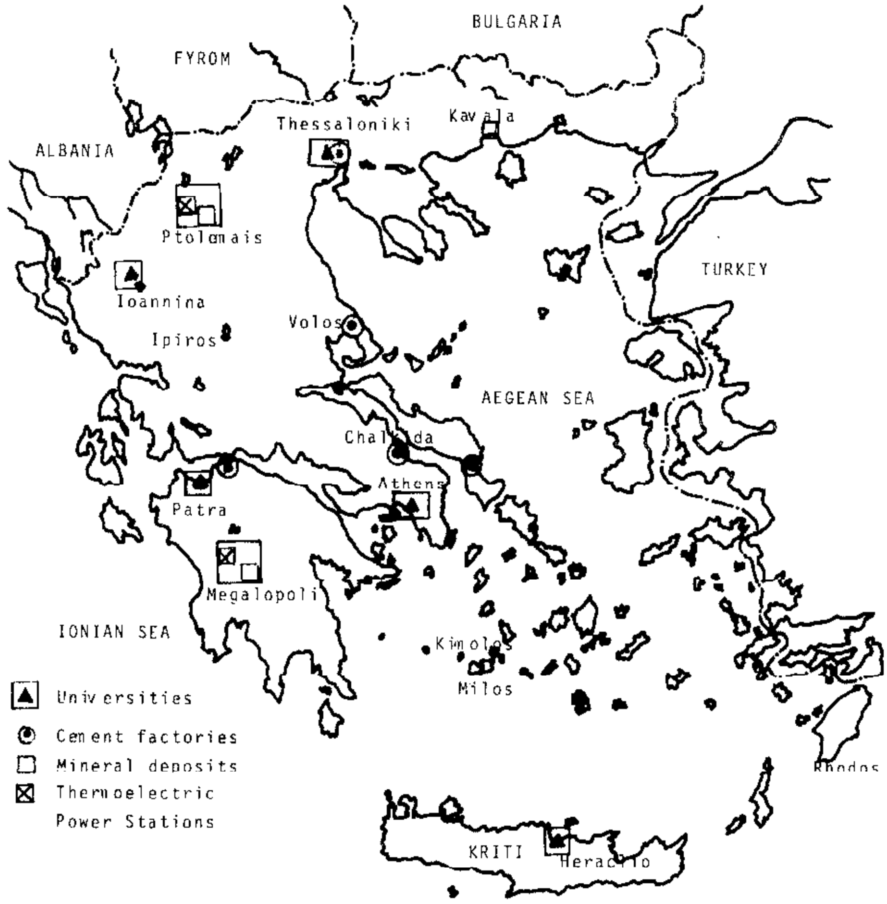

Fig. 1 Greek location map

Separation, recovery and recycling of gases in coal upgrading: Advanced materials from coal

The energy efficiency and the environmental consequences of typical coal upgrading processes, such as combustion and gasification, depend to a large extent on the degree of gas separation, recovery and recycling [21]. Among the available methods used in the chemical and petrochemical industries, the technology of polymeric and ceramic membranes offers several advantages, such as low size, simplicity of operation, compatibility and diversity. To date, the polymeric ones are most efficient and therefore many energy studies have been undertaken with regard to their application in power stations. In the field of ceramic membranes, the studies include the development of ultrathin microporous ceramic lays by the conventional sol-gel technique or the new one of chemical vapour deposition (CVD) and evaluation of their gas properties at elevated temperatures. Application of ceramic membranes for gas separations in power stations requires further development, although their high-temperature separation potential is very promising [22].

The industrial gases are usually separated by conventional processes, such as cryogenic distillation or adsorption. The adsorption processes based on silica gel (ceramic membranes) or the new activated carbon (carbon molecular sieves, CMS) as adsorbents have proven reliable and cost-effective. The CMS are a specially prepared form of activated carbon having average pore dimensions similar to the critical dimensions of small molecules, and combined with the new process of pressure swing adsorption (PSA). Their properties depend upon the initial carbonization and activation procedures. Separations that have been industrially accomplished include: oxygen and nitrogen, carbon dioxide from methane, ethylene from ethane, the removal of solvents and of chlorinated hydrocarbons. The controlled activation of coal is accomplished by conventional and modern technology such as radiofrequency/microwave plasma unit of oxygen (RF/MV plasma), at low temperature. The advanced materials thus prepared, CMS and activated carbon fibres are studied with regard to their pore structure development and the modification of surface functional groups during the thermal treatment of the products.

Pharmaceuticals

Purity determination

The presence of impurities in a sample will cause the melting peak measured by DSC to broaden and to shift to lower temperatures. For pharmaceuticals, for example erythrocytes or organoplatinum antitumour agents, the assessment of purity is very important. The stability, and hence the shelf-life, of pharmaceutical drugs and of dosage mixtures is highly important since the product may become less effective. By using suitable thermal analysis techniques, DSC and hot-stage microscopy, it is possible to aid in testing the active component in drugs and to determine the degradation on melting or the possible polymorphic forms. Their interconversion should involve no mass loss on TG.

DSC is a technique with established importance for study of the thermotropic properties of the lipids in technical and biological membranes, and of the changes caused by the presence of drug molecules in the thermotropic properties of the lipids. Two classes of drug molecules have been investigated, the cannabinoids and the anaesthetic steroids. The profile of the DSC curves depends on the molecules in the membranes. The phospholipids belong in a class of lipids that exhibit large-scale entry into the membranes, and in biological systems always exist in an aqueous environment, where they automatically form solvated bilay-

Table 1 University laboratories and research institutes in Greece

Polymeric materials
Chemical Physics, Chemical Engineering, Aristotle University, Thessaloniki
Organic Chemical Technology, Chemistry, Aristotle University, Thessaloniki
Chemical Physics, National Technical University, Athens
Strength Materials, National Technical University, Athens
Demokritos, Research Institute, Athens
Electronic Structure-Laser Institute, Athens
Government Chemist Laboratory, Athens
Inorganic materials
Inorganic Chemistry, Chemistry, Aristotle University, Thessaloniki
Industrial Chemistry, Chemistry, Ioannina University
Analytical and Inorganic Chemistry, National Technical University, Athens
Mechanical and Aeronautical, Engineering, Patra University
Cement Research Institute, IRAKLIS Co., Athens
Cement Research Institute, TITAN Co., Thessaloniki and Athens
Minerals
Mineralogy and Petrology, Geology, Aristotle University, Thessaloniki
Mineralogy and Petrology, Athens University
Industrial Chemistry, Chemistry, Ioannina University
Analytical and Inorganic Chemistry, National Technical University, Athens
General Chemical Technology, Engineeering, Aristotle University, Thessaloniki
Chemical Process, Engineering Resarch Institute, Thessaloniki
Pharmaceuticals
Organic and Pharmaceutical Chemistry, National Research Institute, Athens

ers. Under these conditions, the phospholipids exhibit two mesomorphic phases: a) the gel, regarded as in the solid state at low temperature, and b) the liquid crystalline phase, where a transformation takes place at higher temperature [23].

Bentonite, a montmorillonite alteration of volcanic ash, is found in the Greek islands Milos and Kimolos. It has the unusual property of expanding to several times its original volume when placed in water, and this fact gives rise to interesting industrial uses such as stopping leakage in soil, rocks and dams. Bentonite, is also called pharmaceutical alumina because it has a multitude of uses. By means of thermal analysis techniques, mainly TG and DSC, an investigation of bentonite properties is undertaken, in order to evaluate and study the possibility of its pharmaceutical applications.

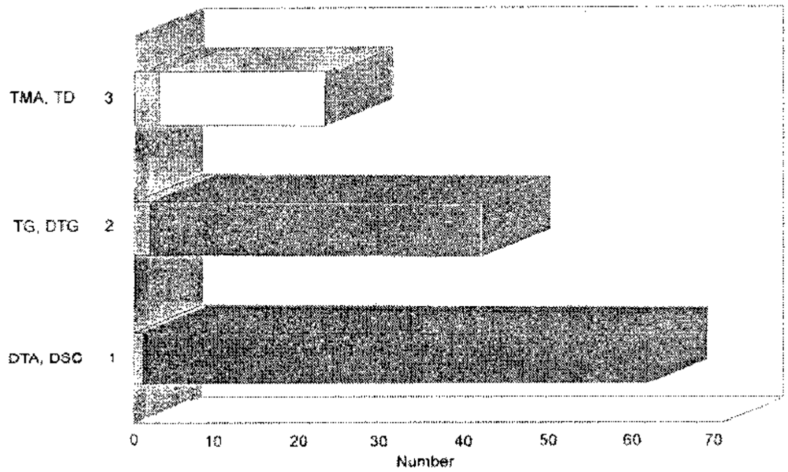

Fig. 2 Numbers of TA instruments in industry institutes and universities

At this point, I would like to mention the university laboratories and research institutes in Greece, dealing with the above-mentioned topics of thermal analysis (Table 1 and Fig. 1). Figure 1 shows the locations of the cement factories and the regionally exploited minerals, together with the local thermoelectric power stations, while Fig. 2 depicts the distribution of thermal analysis instruments. It is believed that an increase in thermal analysis equipment will be achieved in the next few years.

Conclusions

This necessarily brief review may help the reader to have access to Greek scientists working in the field of thermal analysis. The methods used and the applications in several systems are highlighted. Certain aspects have been only sketchily dealt with and would deserve a more detailed description.

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