Nuclear

Thermal analysis and calorimetry solutions

SETARAM Instrumentation

KEP Technologies

Excellence in thermal analysis and calorimetry

Nuclear energy:

Extreme service conditions for very special materials

The energy question is one of the issues that will determine the future of our society. It is necessary to vastly increase the use of nuclear reactors for the production of electricity across the world. Scientists, researchers and industrialists working in the nuclear sector, whether civil or military, are constantly seeking to improve performance and safety. They are confronted with problems of the choice and characterization of highly diverse materials, ranging from glasses and ceramics or metals and special alloys to concretes and bitumens. These are the materials used in the industrial process, in each stage of the nuclear energy cycle. Their characterization is all the more delicate and important in that they must withstand highly particular service constraints, namely nuclear radiation, high pressure, high temperature and thermal shock.

The question of the management of radioactive waste is critical. Radioactive material can present real hazards, and storage facilities must be designed to adequately control these hazards. It is in this respect that the evaluation of the quantity of radioactive elements (curium, tritium, plutonium) contained in storage or reprocessing containers is of crucial importance in order to optimize the nature of the protection.

Nuclear power cycle and electricity transmission and distribution (AREVA)

SETARAM instrumentation proposes solutions for the research and thermal characterization of materials, and for the quantification of radioactive elements throughout the civil nuclear energy sector:

- from the extraction of uranium ore to the recycling of spent fuel
- in the treatment of waste,
- in the conversion and enrichment of uranium, the manufacture of fuel, the design of reactors, etc.

What material characterization problems are encountered in the nuclear sector?

High temperatures (up to 2400°C), corrosive gases, damp atmospheres, large volumes, radiation, placing in glove boxes or hot cells… the characterization of materials for nuclear applications demands thermal analysis and calorimetry instruments that sometimes have to be made to measure.

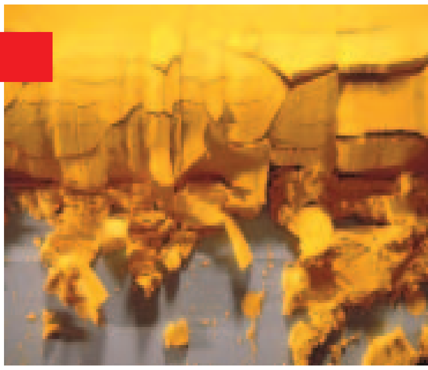
Extraction and processing of uranium ore

Mc Clean Lake JEB. Saskatchewan. Canada.
AREVA/DARKHORSESTUDIO

Uranium in pure form is a hard gray metal. It is never found in its native metal form, but as an ore in proportions of 3 grams per tonne on average. Once the ore has been extracted it undergoes a series of mechanical (crushing) and chemical (alkaline or acid attack) treatments to bring it into solution, followed by separation of the uranium-containing solution and the sandy residues, and precipitation of the uranium as uranate or uranium peroxide which gives a yellow powder called "yellow cake" once dried.

The optimization of this transformation process requires thermal analysis tools that function in different gaseous atmospheres.

Uranium conversion and enrichment



Yellowcake on a belt filter at the ore processing plant operated by Société des Mines de Jouac (SMJ). Haute-Vienne Department. France
AREVA/LESAGE (PHILIPPE)

The yellow cake cannot be used as a nuclear fuel in its pure form; it must first be enriched. It therefore undergoes a series of chemical treatments under fluorine. After a purification step, the concentrate is transformed into uranium tetrafluoride UF_4 which in turn is transformed into UF_6. This compound has the particularity of changing from the solid state to the liquid or gaseous state under small temperature changes. In gaseous form at 65°C, the UF_6 is perfectly suited to the subsequent phase of enrichment (increase in the concentration of the ^{235}U isotope to the detriment of the ^{238}U isotope) by gaseous diffusion or centrifuging.

The optimization of this enrichment process requires thermal analysis tools functioning at high temperature (2400°C) in an atmosphere of hydrogen fluoride, a corrosive gas. The instrument is often placed in a glove box, making it necessary to separate the control and acquisition electronics from the measurement section.

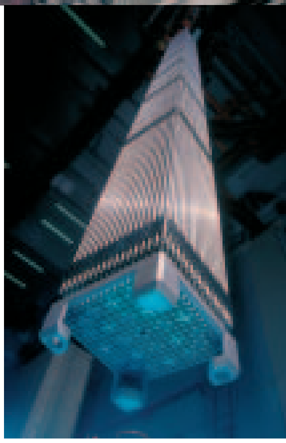
Inspection of Mox fuel pellets, Mox fuel fabrication plant, ATPU. Cogema-Cadarache. 1994. France. AREVA/LESAGE (PHILIPPE)

Fuel fabrication

After defluorination the [235]U enriched uranium takes the form of an oxide powder (UO_2) that is highly compressed to produce small pellets which are then sintered (at about 1700°C in H_2 atmosphere).

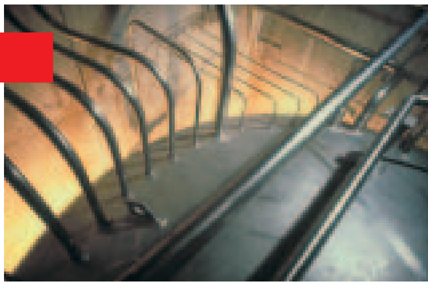
These UO_2 pellets are then introduced into long metal tubes made from a zirconium alloy (**Zircalloy**), is chosen because it is transparent to neutrons and does not slow down the nuclear reactions within the reactor core. These zirconium tubes also constitute an initial sealing barrier and must withstand high mechanical and thermal stresses, by preventing the transfer of radioactive products to the exterior.

The development of these processes using **uranium oxides** (ceramic) and **Zircalloy** (alloy), and the simulation of long-term behavior (corrosion, oxidation) require thermal characterization tools operating at high temperatures in highly specific atmospheres (corrosive gases, water, etc.).



Mox fuel assembly, Melox fuel fabrication plant. Bagnols-sur-Cèze. France. AREVA/LESAGE (PHILIPPE)

Reactor design - Reactor vessel metallurgy



Fission product sampling tank, T2 high-level separations facility, UP3 reprocessing plant, Cogema-La Hague. Cherbourg. France. AREVA/JEZEQUEL (SIDNEY)

BWRs (boiling water reactor) or PWRs (pressurized water reactors) have a vessel containing the reactor core with the fuel. The self-sustained chain fission reaction heats the vessel and the water in contact with the reactor walls.

The longevity of the vessel (aging, corrosion, material compatibility and oxidation) is a strategic factor in the safety of nuclear power plants.

Spent fuel recycling

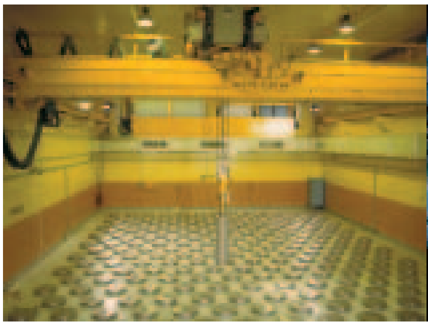
The uranium or plutonium contained in the spent fuel is recycled. A very large percentage can be recycled as MOX (mixture of uranium and plutonium oxides) which in turn is used as fuel, after in-depth analysis at high temperature (up to 2400 °C).

Eurodif's Georges Besse enrichment plant. Tricastin. France. AREVA/LESAGE (PHILIPPE)

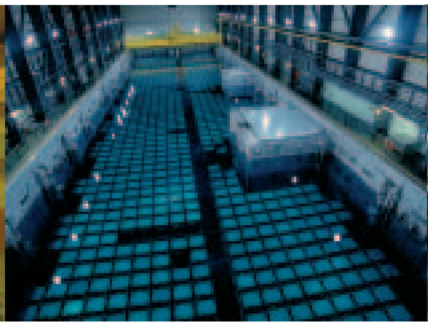
Nuclear waste management

Nuclear waste materials are immersed in bitumen-, concrete-, glass- or ceramic-based matrices depending on their radioactive activity and half-life, which are then stored in special stainless steel drums and (in the case of high-activity waste) immersed in a spent fuel pit. To ensure the longevity of these drums, the researchers and manufacturers study the compatibility of materials and their degradation under conditions of intense radiation.

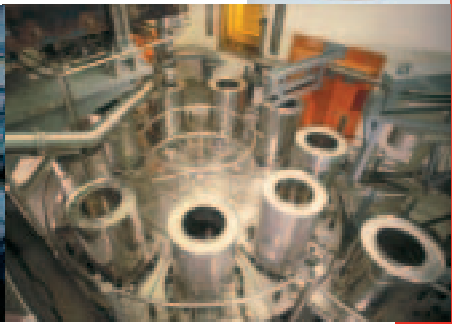
Cutaway of a glass canister, UP2 800 reprocessing plant, Cogema-La Hague. Cherbourg. France. AREVA/LESAGE (PHILIPPE)



Basket transfer by bridge crane in the handling area, Cascad dry storage facility for spent fuel and waste. CEA-Cadarache. Saint-Paul-lez-Durance. France. AREVA/JEZEQUEL (SIDNEY)



Spent fuel storage pool. COGEMA-La Hague reprocessing plant. Cherbourg. France. MAGNUM/GRUYAERT (HARRY)



Drum pouring turntable, STE3 liquid effluent treatment station, Cogema-La Hague reprocessing plant. Cherbourg. France. AREVA/JEZEQUEL (SIDNEY)

In the case of military applications, as ^{239}Pu has a half-life of 24,110 years it is constantly being recycled and reconditioned, requiring constant quantitative monitoring.

Tritium, a radioactive isotope of hydrogen, is also present in some waste. It has a half-life of 12.5 years and is very difficult to quantify by its weight, but the heat emitted gives a very good indication of its radioactive activity.

Thermal analysis and calorimetry for nuclear applications

When a material is heated or cooled, its structure and its chemical composition undergo changes, such as melting, crystallization, oxidation, reduction, decomposition, reaction, transition, expansion or sintering. A radioactive material (and radioactive waste in particular) emits heat .

Thermal analysis and calorimetry are ideal means for characterizing these materials.

SETARAM instrumentation proposes a global solution of thermal analysis and calorimetry (heat measurement) instruments for nuclear research and industry. These instruments have numerous applications in the nuclear sector:

- Material studies: behavior of materials as a function of temperature (at a given pressure, possibly in damp, gaseous or corrosive atmospheres).
- Quantification of the material: the instrument determines the quantity of nuclear material present (in a container for example) by measuring the heat emitted.
- Measurement of thermal activity: the instrument determines whether the container (containing a radioactive material) is subject to a tolerable thermal power level.

Physical property studied	Technique
Weight	Thermogravimetric Analysis (TGA)
Temperature	Differential Thermal Analysis (DTA)
Enthalpy	Differential Scanning Calorimetry (DSC)
Dimensions, mechanical characteristics	Thermomechanical Analysis (TMA)
Radiation (emission of heat)	Calorimetry

SETARAM instrumentation: world leader in thermal analysis instruments for nuclear research and industrial applications

The wide range of instruments for the nuclear industry results from a longstanding relationship with the French CEA (Commissariat à l'Energie Atomique – Atomic Energy Commission), a highly demanding customer with very stringent requirements in terms of performance and precision.

SETARAM instrumentation's overall offering for the nuclear sector is both extensive and suited to its specific needs. Compared with competing product offerings, SETARAM instrumentation's solutions permit **higher temperatures** (2400°C), **larger volumes** (up to 400L !), **excellent sensitivity** and reliability of measurement (particularly thanks to the Calvet three-dimensional calorimeter 3D-Sensor Inside). But that's not all: the instruments can be equipped for the analysis of materials in damp or corrosive atmospheres.

3D sensor inside

The great **modularity** of the instruments means that users can make substantial savings with their investments. And this modularity applies throughout the lifetime of the instrument, not just when making the initial purchase, with numerous options that can be added as and when required.

SETARAM instrumentation moreover proposes a number of essential services to meet the growing needs in the nuclear sector. The sharing of skills allows the appropriate instrument and solution for a given application to be proposed: **"made-to-measure"** instruments. This can be either a modified standard product (electronic circuitry separate from the measuring head which will be placed in a hot cell, for example), or an instrument with a specifically tailored design to respond optimally to the need.

Customized solutions

In addition, the worldwide presence of SETARAM instrumentation (particularly through its network of agents and distributors) greatly facilitates its participation in international projects and partnerships (in Europe and the Far East in particular).

SETARAM instrumentation continues to develop new solutions (instruments, software, etc.) for nuclear applications so as to increase the performance of an industry that is always seeking means of speeding up its studies and developments, lowering its costs and guaranteeing its reliability.

Sample storage cell, analytical laboratory, UP3 reprocessing plant, Cogema-La Hague. Cherbourg. France. AREVA/JEZEQUEL (SIDNEY)

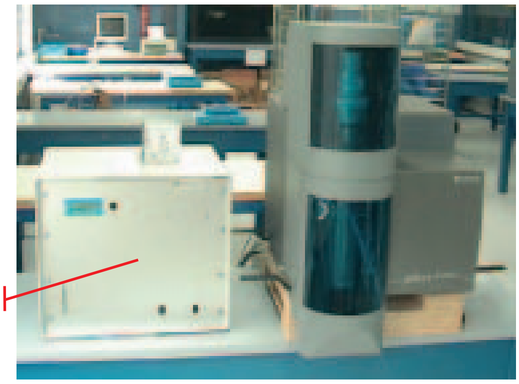
The SETARAM instrumentation product offering for the nuclear sector

SETSYS Evolution: the top of the range in high-temperature thermal analyzers

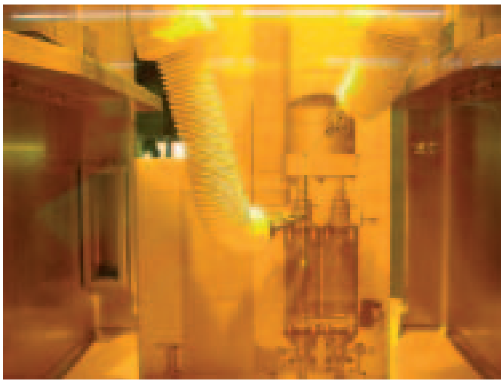
SETSYS Evolution

- Temperature range: **-150°C to 2400°C, the ambient/2400°C range is covered by a single oven**
- **Modular system**: DTA, DSC, TGA, TMA adapting interchangeably on the same structure
- **High-precision balance** placed in high position, available in two weighing capacities: 35g or 100g
- Simultaneous **TGA-DTA** measurements **up to 2400°C, TGA-DSC up to 1600°C**
- **TGA-EGA**: Coupling with MS, FTIR, GC, etc. gas analyzers by either thermoregulated capillary or the "Supersonic System" (sampling by supersonic expansion) for mass spectrometry measurements of up to 1024 amu (heavy or condensable molecules)
- **Measurements in varied and controlled atmospheres**
  - → Controlled introduction of one gas or a mixture of two gases
  - → Possibility of measuring in corrosive atmosphere
  - → Possibility of measuring in damp atmosphere using the **Wetsys** controlled humidity generator
  - → Possibility of establishing a high-level vacuum in the analysis chamber (up to 0.01 Pa /10^{-4} Torr)
- Controlled speed thermal analysis: in TGA version, temperature control possible according to the decomposition of the sample
- In the TMA version, possibility of temperature control according to the speed of sample sintering
- **Can be placed in a glove box or hot cell (option already adopted by several customers)**

Separated electronic box



SETSYS Evolution designed for installation in a glove box or hot cell: the electronic circuitry is installed in a separate remote box to prevent it being exposed to the radiation.



"Customized" **SETSYS** placed in a hot cell

96 Line, the modular system of large-volume high-temperature thermal analyzers

3D sensor inside

- Temperature range: **ambient to 2100°C**
- **Modular system**: DTA, DSC, TGA, TMA, calorimetric modules adapting interchangeably on the same structure
- **High temperature up to 2100°C**
- **Large sample volume available**
- Possibility of coupling with gas analyzer
- **Accurate calorimetric measurements from ambient temperature to 1500°C** (for heat capacity (**Cp**) measurement in particular)
- Drop calorimetry for process simulation (alloy for instance)
- Varied and controlled atmospheres
- **Can be placed in a glove box or hot cell (option already adopted by several customers)**

96 Line
MHTC 96 calorimeter version

C80, the mixing and reaction calorimeter

3D sensor inside

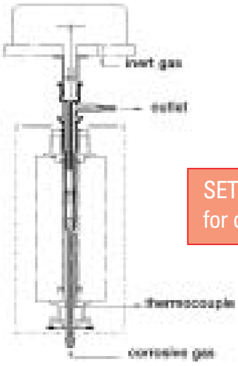
- Temperature range: **ambient to 300°C**
- **Mixing** and **reaction** calorimeter
- **In-situ calorimetric measurements** possible on mixtures, solid or liquid interactions with liquid or gas
- Uses the SETARAM Instrumentation's exclusive **3D-Sensor** calorimetric sensor
- Joule effect calibration for **precise and sensitive calorimetry measurement**
- **Can be placed in a glove box or hot cell (option already adopted by several customers)**
- Other calorimeters of similar design to the C80 (using the 3D-Sensor technology) are available for different temperature ranges:
  - BT2.15 calorimeter: from -196 to 200°C
  - MS80 calorimeter: from ambient temperature to 200°C
  - HT1000 calorimeter: from ambient temperature to 1000°C

C80 Calorimeter

APPLICATIONS

Uranium conversion and enrichment

Thanks to its possibilities of measuring **high temperatures** of up to **2400°C**, remoting the electronic circuitry so that the instrument can be placed in a **glove box**, and its specific accessory for taking **thermogravimetric measurements in HF atmosphere**, the **SETSYS Evolution** is used for taking measurements on fluorinated uranium compounds.



SETSYS Evolution accessory for corrosive gas atmosphere

Fuel fabrication

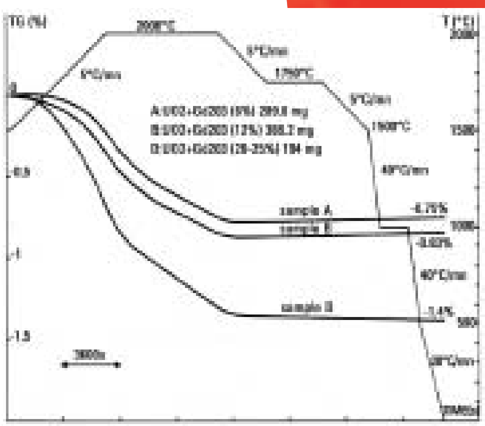
Several SETARAM instrumentation systems are used to characterize the materials present in the fuel (uranium oxide, Zircalloy, etc.).

For uranium oxides,

- Stoichiometric studies, long-duration isothermal measurements, sintering studies are ensured by a modular high-temperature system (possibility of measuring TGA, DTA, DSC and TMA) such as **SETSYS Evolution**
- Heat capacity (Cp) measurements are carried out using the **MHTC 96**, the most suitable instrument in the **96 Line** for taking accurate Cp measurements at high temperature

The following SETARAM instrumentation systems are particularly well suited to the characterization of Zircalloy and its reactivity with respect to water, gases and metals:

- **SETSYS Evolution**, thanks to its high temperature range, the possibility of coupling it to the WETSYS controlled humidity generator allowing thermogravimetric measurements in damp atmospheres, and its highly sensitive balance that can detect very small weight gains or losses
- The **96 Line** in the MHTC96 calorimeter version that can measure the heats of dissolution of a metal in an alloy by drop calorimetry
- The **C80 calorimeter** for all the measurements for obtaining thermodynamic data which, thanks to the three-dimensional design of its "3D-Sensor Inside", can determine heats of reaction, of mixing, and thermal capacities with unparalleled precision.



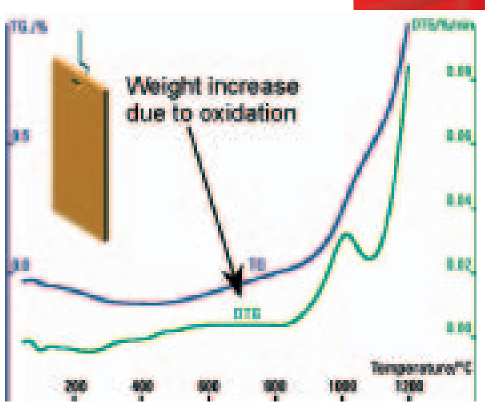
Stability of uranium oxide at 2000°C – High-temperature Thermobalance

A UO_2 powder used as a nuclear fuel is mixed with gadolinium (Gd_2O_3), a neutron collector. The standard utilization temperature for this mix is 1600°C, but it is interesting to examine the impact of increasing the temperature to 2000°C.
A loss of weight corresponding to the giving off of oxygen occurs at 1700°C. The weight subsequently decreases during the isothermal phase at 2000°C (2 hours).
The total weight loss is proportional to the percentage of Gd_2O_3.

Reactor design
Reactor vessel metallurgy

The characterizing of the metals and special alloys used in the design of reactor vessels requires the use of:

- The complete **SETSYS Evolution** product line (TGA, TGA-DTA /DSC, TMA, TGA-EGA) for its high-temperature capabilities, its measurement sensitivity, the possibilities of taking measurements in diverse atmospheres (wet, corrosive, reducing, etc.).
- The C80 calorimeter for its versatility, which enables all necessary thermodynamic data to be determined.



Corrosion of a steel - Setsys Evolution
The metal is directly suspended from the balance to ensure better interaction with the air and a greater study surface area.

Large-volume calorimetry for characterizing nuclear waste.

Calorimetry, as its name indicates, is the measurement of heat. A calorimeter measures any transfer of thermal energy from an object to its surrounding environment.

When a container contains a radioactive waste material emitting α and β nuclear radiation (curium, plutonium, tritium, etc.), it emits a quantity of heat proportional to the quantity of that radioactive material. This quantity of heat can be quantified using a calorimeter. SETARAM instrumentation's large-volume calorimeters (from 1L to 400L) can detect thermal radiation levels of just a few µW. These calorimeters can be adapted to any size of waste drum and can be installed in glove boxes.

Advantages

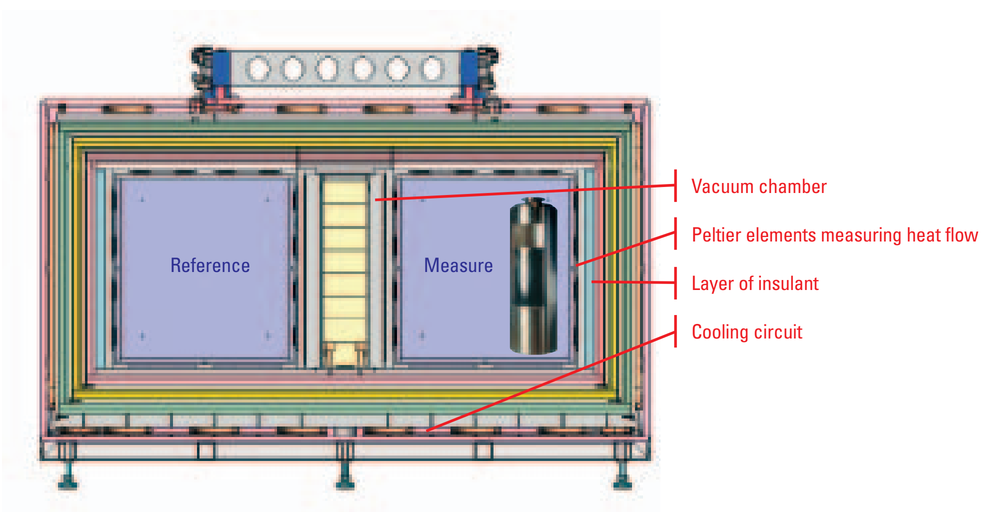
- Precision of measurement, no matrix or absorption effect
- Ease of signal interpretation and simplicity of processing
- Ease of calibration
- Low cost compared with other methods, no maintenance costs
- Safety of use, no need to process the sample, little human exposure to the object
- Non-destructive method
- Method complementary to gamma spectrometry

General principle

The calorimeter is of the twin-cell symmetrical heat flow type. It consists of a thermostat-controlled block, opening at the top and surrounding two wells (cavities), each designed to receive a container. One cavity – the sample or measuring chamber – is loaded with an active product, while the other – the reference chamber – is left empty or loaded with an inactive product .

The six surfaces of each cavity are covered with flowmetric plates (Peltier elements) that can measure an electrical signal (e.m.f.) proportional to the heat flow between the interior of the chamber and the thermostated block.

As the Peltier elements cover all six surfaces, virtually all the heat flow produced in the chamber and transmitted to the exterior can be integrated.



Cross section of large-volume calorimeter

Example of specifications

(contact us to find the ideal solution to meet your needs).

	390	680
Internal volume	60 liters	90 liters
Closed calorimeter		
Height/Width/Depth (mm)	960 / 1500 / 1000	1260 / 1500 / 1000
Approximate weight	1000 kg	1200 kg
PERFORMANCE		
Detection limit	457 µW	970 µW
Measurement range	0.5 – 13000 mW	1 – 26000 mW
Sensitivity	160 µV/mW	155 µV/mW
Time constant	5 hours	
Working temperature (isothermal)	< 40°C	

APPLICATIONS

Vitrification

The fission products are mixed with a vitrifying matrix and melted in a furnace. The resulting module, by virtue of the activity of the nuclear materials introduced, produces a large quantity of heat. This must not exceed a given level beyond which self-melting can occur.

If the gamma spectrometry in principle enables a quantity of radioactive material to be evaluated, it is unsuitable for this type of problem:

- the kinetic energy of the α and β radiation is much higher than the radiation.
- the material is not homogenous, and the evaluation of the α and β rays from the measurement of the γ rays is very imprecise.

Calorimetry is the most accurate method because one obtains the thermal power of the module directly. The calorimeter can be installed in a hot cell between the spent fuel pit and the vitrification line.

Waste accounting

The waste from the dismantling of equipment facilities or consumables containing residues of radioactive material is subject to rigorous accounting. Conventional methods of measuring radiation (γ, neutrons) are very often sensitive to the problems of attenuation due to the matrix of the package in which the radioactive material is disseminated among assorted objects (glass, plastics, metal, etc.). As these objects cannot absorb the heat produced by the radioactive material, calorimetry represents the ideal measuring method. The coupling of gamma spectrometry and calorimetry can by used to determine the isotopic composition and the quantity of radioactive species respectively.

Cigar Lake underground mine. Saskatchewan. Canada. AREVA/DARKHORSESTUDIO

Some of our references

ABB - Sweden
AIST (Advanced Industrial Science & Technology) - Japan
ARZAMAS - Russia
BATAN (Indonesian National Nuclear Energy Agency) - Indonesia
BARC (Bhabha Atomic Research Center) - India
BNFL - UK
CEA (Commissariat à l'Energie Atomique) - France
CEN - Syria
CERN (European Organization for Nuclear Research) - Switzerland
COGEMA - France
COMHUREX - France
CTMSP (Centro Tecnológico da Marinha em São Paulo) - Brazil
EDF - France
EURATOM - Italy, Germany
FBFC - Belgium
Forschungszentrum Jülich - Germany
IGCAR (Indira Ganghi Centre for Atomic Research) - India
ININ (Instituto Nacional de Investigaciones Nucleares) - Mexico
INER (Institute of Nuclear Energy Research) - Taiwan
IPEN (Instituto de Pesquisas Energéticas e Nucleares) - Brazil
JAERI (Japan Atomic Energy Research Institut) - Japan
JNFL (Japan Nuclear Fuel Limited) - Japan
KAPL - USA
Korea Atomic Energy Research Institute - Korea
LANL (Los Alamos National Laboratory) - USA
NECSA (South African Nuclear Energy Corporation) - South Africa
NUCLEAR FUEL COMPLEX - India
ORNL (Oak Ridge National Laboratory) - USA
SCK – CEN (Centre d'Etudes de l'Energie Nucléaire) - Belgium
STUDSVIK A.B - Sweden
WESTINGHOUSE - USA

Specifications are given as indications only and are not contractual - 08/05

Naturine RCS LYON B 389 392 929

SETARAM Instrumentation
KEP Technologies

SETARAM INSTRUMENTATION
7, rue de l'Oratoire
69300 Caluire - France
Phone +33(0)4 72 10 25 25
Fax +33(0)4 78 28 63 55

SETARAM Inc.
7905 Browning Rd, Suite 206
Pennsauken N J 08109-4323 - USA
Phone +1 856 910 9990
Fax +1 856 910 1150

sales@setaram.com - www.setaram.com

A KEP Technologies Company

KEP TECHNOLOGIES