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REVIEW

BOMB CALORIMETERS FOR DETERMINATION OF THE SPECIFIC COMBUSTION HEAT OF FUELS

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Presently, due to commercialization and decentralization of the fuel shipment system in the former USSR countries, the quality control of the fuel used in power engineering and on industrial enterprizes has grown sharply in importance. In order to carry out quality control, reliable and convenient measuring instruments are required.

The specific heat of combustion (SHC) is the main power-engineering characteristic of fuel quality. Two main groups of methods for its determination – theoretical (analytical) and calorimetric (experimental) – are known [1]. The former require preliminary chemical analysis of the elemental composition of the fuel and, being indirect, do not provide high accuracy; the latter are based on experimental determination of the SHC and are most reliable and accurate [2]. Special devices, *combustion calorimeters* (CC), characterized by large values of the heat release (40–50 kJ) and a relatively high accuracy have been developed for measurements of the SHC. They are most widespread since they are used not only for regular determination of the SHC on thermal power stations and boiler shops of enterprises, but also in tests of products of chemical and petroleum processing industry, at sites of production and transport of natural fuels, in metallurgy, and in scientific investigations.

Depending on the conditions and duration of the fuel combustion process, bomb calorimeters with the discrete (periodic) operation and continuously operating flame calorimeters are distinguished [3-7]. In bomb CCs, combustion of a fuel sample with a known weight (or volume in the case of a gaseous fuel) takes place in a special reaction vessel, Berthelot calorimetric bomb (CB), in an atmosphere of compressed oxygen at a constant volume. In flame calorimeters, the fuel burns continuously in a chamber connected to the atmosphere. In this case, combustion takes place at a constant pressure. Flame CCs are used in investigations of gaseous or low-boiling liquid substances, whereas bomb calorimeters are used for all types of organic fuel.

The thermotechnical scheme of any bomb calorimeter contains the following three structural elements: 1) kernel of the calorimetric system, consisting, as a rule, of a CB and heat-absorbing body, liquid or solid; 2) shell of the calorimetric system, which provides the necessary regime of the heat transfer to the environment; 3) thermal connection, providing the necessary regime of the heat transfer between the kernel and the shell of the system.

Primary transformers of the temperature and/or heat flux used for maintaining thermal regimes and obtaining the information from measurements when evaluating the SHC are also important construction elements.

The calorimetric bomb is a cylindrical vessel of stainless steel with a cover and has a volume of about 300 cm^3 [1]. Depending on the method of sealing, the CB cover can be self-sealing or not. In the former case, the CB is equipped with a rubber ring that, when compressed between the cover and union nut due to the action of the excess pressure of gases, seals the bomb's cover. In the latter case, sealing is carried out using a lead ring, and the edge of the bomb's vessel bites into the ring when the cover is tightened. Two nipples with valves or vents are provided for filling with oxygen under pressure and evacuation of gaseous combustion products. A holder which fixes a crucible with a fuel sample is attached to the inner side of the cover. The nipples and the holder serve also as conducting elements that deliver current to a thin wire, which is used for fuel ignition.

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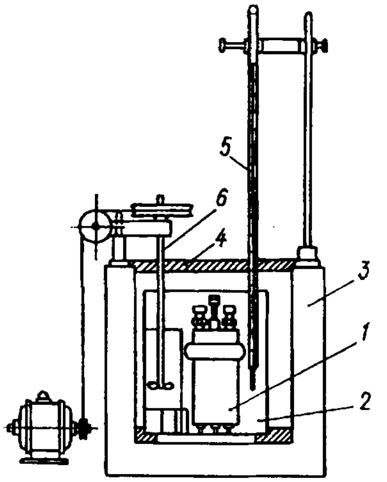

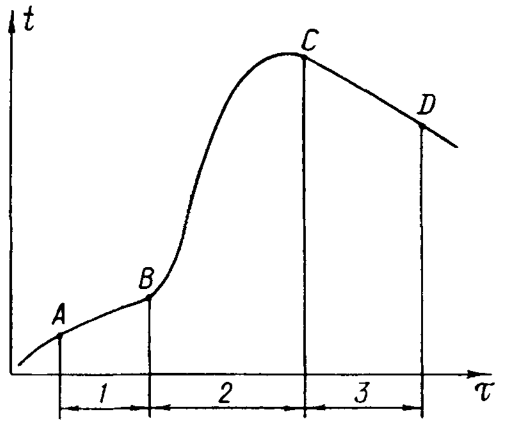

Fig. 1. Liquid isoperibolic calorimeter: 1) calorimetric bomb (CB), 2) calorimetric vessel, 3) casing, 4) cover, 5) thermometer, 6) mixer.

Fig. 2. Character of temperature variations in a calorimetric experiment.

Other types of CBs are also used [7, 8]. However, all of them should provide standard combustion conditions regarding the initial oxygen pressure (3.04 MPa at a temperature of 298 K) and the ratio of the weight of the sample of the substance and the volume (3 g fuel per 1 liter of CB volume).

In what follows, we consider various types of thermotechnical schemes and designs of bomb CCs with examples of particular technical realizations. Their main parameters are presented in Table 1.

Liquid calorimeters with an isothermal shell (also known as isoperibolic). Presently, they constitute the most widespread type of bomb CCs. In these devices, the heat released during the combustion of a fuel sample in the CB is transferred by means of conductive and convective heat transfer to the working liquid, whose weight and specific heat are known. The heat release is determined from the increase in the temperature of the working liquid (usually distilled water). Conditions of the heat transfer between the calorimetric vessel containing the working liquid and the environment are stabilized by means of an isothermal shell. An overall view of a typical liquid isoperibolic calorimeter is presented in Fig. 1.

Calorimetric vessel 2 with a volume of 2000 to 4000 cm^3 with a strong bottom is manufactured from thin sheet brass and is isolated from the cover bottom by a thermoinsulating background glass or plastic, which contacts the vessel only at a few points.

Isothermic shell 3 is usually a massive double-walled metal vessel with a double bottom which is filled with water, which provides protection of the calorimetric vessel from the influence of air flows and oscillations of the temperature of the environment. A mercury thermometer and a mixer are introduced into the calorimetric vessel through the shell cover. Water mixing in shell 3 is also provided in certain CCs. The V-08-M calorimeter (Table 1, item 1) additionally includes a coil pipe for water cooling and electric heaters for setting up the water temperature in the calorimetric vessel and shell before measurements. Owing to this, all measurements are carried out within a narrow temperature region.

An experimental thermogram characteristic of various types of enthalpy bomb CCs is presented in Fig. 2. The calorimetric experiment is usually divided into the three periods [1, 2, 8]: 1) the initial period that precedes burning of the sample, which serves for taking into account the heat exchange between the calorimetric vessel with the environment under conditions of the initial temperature of the experiment, 2) the main period, during which the combustion of the sample, removal of the released heat by the calorinetric liquid, and equilibration of the temperature in the calorimetric vessel take place, and 3) the final period, serving for evaluation of the heat exchange at the final temperature of the experiment.

During the initial period, when the temperature of water in the calorimetric vessel increases linearly due to the heat transfer from the shell (point *A*), the temperature is measured each 30 sec. After 5 to 10 measurements, the ignition circuit is switched on (point *B*). During the main period (*B* – *C*), the temperature is monitored and

TABLE 1. Technical Characteristics of Combustion Calorimeters

No.	Model and thermotechnical scheme of device	Range of measurements, kJ	Error in evaluation, %		Duration of experiment, h	Dimensions, mm (weight, kg), method of information processing	Company, country, reference
			effective heat capacity	SHC			
1.	V-08-M LI	20–40	0.1	–	0.33	420 × 370 × 720 (50), NA	USSR [1, 10]
2.	V-08-MA LI	20–40	0.1	–	0.33	500 × 350 × 870 325 × 340 × 220 (90), NA	"Etalon" factory, Almaty, Kazakhstan [11, 12]
3.	V-08-MB LI	20–40	0.1	–	0.33	706 × 442 × 532 485 × 393 × 170 320 × 317 × 150 (140), A	State Special Design Department of Thermophysical Instrumentation, Russia [13, 14]
4.	CA-3 LI	4–31	0.5	–	0.5	600 × 490 × 1250 (78), A	Shimadzu Corp., Japan [14, 15]
5.	Parr-1261 LI	–	–	–	0.1	500 × 375 × 350 (–), A	Parr Instruments, USA [16]
6.	AS-200 LI	0.12–35	–	0.1	0.25	1546 × 1780 × 533 (140), A	Leco Corp., USA [3, 14]
7.	OQ-203 LA	up to 30	–	–	–	610 × 335 × 525 (–), NA	Labor MIM, Hungary [17]
8.	IKA-C400 LA	20–40	0.1	–	0.5	300 × 470 × 280 (90), A	Janke & Kunkel GmbH, Germany [14, 18]
9.	IKA-C700T MIS	–	–	0.1	0.05	– (–), A	Janke & Kunkel GmbH, Germany [14, 19]
10.	KTS-1 KTS-2 CI	10–40	–	0.2	1	Ø 300 × 820 370 × 300 × 105 (40)	Institute for Problems of Energy Saving of the National Academy of Sciences of Ukraine, "Shtorm"Design Department, Ukraine [20]

Note: LI, liquid isoperibolic; LA, liquid adiabatic; MIS, massive with insulating shell; CI, conductive isoperbolic; A, automated information processing; NA, nonautomated information processing; – , information not available.

measured continuously. In the first 30 sec, the temperature varies insignificantly, then grows rapidly, reaches its maximum, and starts to decrease. The following time period ($C - D$), when the temperature decreases linearly, is related to the final period of measurements. The specific heat of combustion q of the sample under investigation is calculated by the formula [1]

$$q = \frac{KH\,[(t_{\text{end}} + h_{\text{end}}) - (t_{\text{start}} + h_{\text{start}}) + \Delta t] - q_1 G_1}{G},$$

where Δt is the correction for the heat transfer given by the following expression:

$$\Delta t = (V_1 + V_2)\, b/2 + V_2 r .$$

The correction for the heat transfer can also be calculated by other methods. The Dickinson and Regnault–Pfaundler formulas and other expressions are known [2].

The thermal equivalent K of the calorimeter is determined during the metrological certification of the device and is periodically verified by combustion of a reference substance, benzoic acid [5].

In precision measurements, the electric ignition energy and the heat of dissolution of acids formed upon combustion of the fuel are subtracted from the total quantity of heat released in the CB.

Various types of primary temperature transformers are used for measurements of the water temperature in the calorimetric vessel in different CCs. For example, a metastatic thermometer with scale divisions of 0.01 K is used in the V-08-M calorimeter [10]. Inasmuch as the temperature should be measured with a resolution of not less than 0.001 K, an optical device enters into the construction of the calorimeter, through which an operator divides the distance between readings of the scale into 10 equal parts by eye, which provides temperature measurements with the required accuracy. This method of temperature measurement is rather laborious and is subject to a high degree to personal equations of the operator. This drawback has been overcome in the V-08-MA calorimeter (Table 1, item 2), where a platinum resistance thermometer is used for temperature measurements along with a metastatic thermometer. The resistance is measured using standard electric gages which complete the CC.

The V-08-MB calorimeter (Table 1, item 3) also includes platinum resistance thermometers in a bridge connection. The control of a calorimetric experiment, recording of data, data processing, and output of results are carried out automatically using a microprocessor-based control system. Two models of the V-08-MB calorimeter, for a gaseous fuel and solid and liquid fuels, have been developed.

Isoperibolic liquid CCs are also produced by a number of foreign companies. Their design utilizes a similar thermotechnical scheme but is characterized by a high level of automation of the processes of preparation for and carrying out of the experiment, measurements and experimental data processing, and the presence of diversified service equipment. The use of several interchangeable CBs and autonomous systems for preparation of distilled water and stabilization of its temperature makes it possible to improve substantially the efficiency when carrying out large-scale technical measurements.

The process of measurements is fully automated in the CA-3 bomb calorimeter produced by Shimadzu Corp. (Japan) (Table 1, item 4). The water temperature in the calorimetric vessel is continuously monitored on a digital display. A printing device is used to make a record of readings of a digital temperature gage during ignition of the sample and after ignition in 30-sec intervals during the rise of the temperature and in the final stage of measurements. The water temperature in the calorimetric vessel is measured by platinum resistance thermometers, and the temperature differences between the calorimetric vessel and the shell and between the shell and the surrounding air are measured by nickel resistance thermometers.

The bomb calorimetric system Parr-1261 produced by Parr Instruments (USA) (Table 1, item 5) is equipped, in addition to a main calorimeter, by various service devices: printer, additional oxygen cylinder, water thermostat, water cooler, and automated chemical analyzer. To ensure minimum heat losses and long-term service, the external housing and the water shell of the calorimeter are made of a high-durability glass-cloth-reinforced crude rubber. A microprocessor collects and processes the information, i.e., monitors the temperature of the shell, temperature variations, takes into account heat losses, and, upon completing the measurements, receives information on the content of acids and sulfur in combustion products from the chemical analyzer. An RS-232C interface provides communication of the microprocessor with a standard printer. A built-in back-up battery is included to provide information protection in cases of troubles with the conventional power supply. The temperature in the calorimetric vessel is measured using a high-accuracy electronic sensor with a resolution down to 0.0001 K. The CA-3 and Parr-1261 calorimeters can be used for determination of not only the SHC, but also the caloric value of food products and heats of combustion of various substances.

Leco Corp. (USA) produces the AC-200 multibomb isoperibolic system (Table 1, item 6), which can operate as a system with one, two, or three vessels, which enables an operator to analyze up to 15 samples per hour. The system operation is fully automated: a microprocessor controls the temperature of the calorimetric vessel filled with water, carries out ignition of the sample, stores data and corrects them with respect to heat losses by the Dickinson formula [2, 8]. The value of the specific heat of combustion is output on a digital display and printer.

Adabatic Liquid CCs. Heat losses in the calorimetric vessel is a common drawback of all models of isoperibolic CCs. In order to take them into account and evaluate corresponding corrections, one should to monitor the entire processes of temperature changes both before the ignition of the fuel and after its combustion and completion of the heat transfer between the CB and liquid in the calorimetric vessel. The adiabatic operation mode, during which the temperature of the CC shell is maintained exactly equal to the temperature of the working liquid,

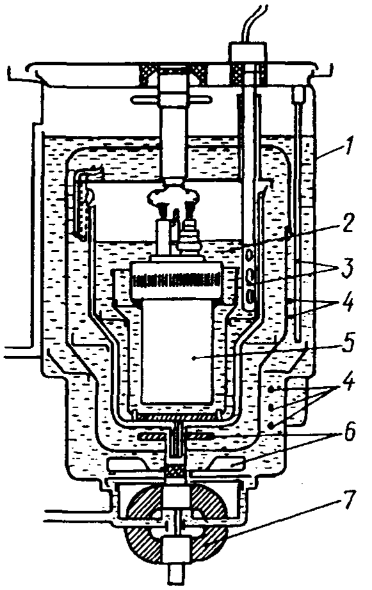

Fig. 3. Liquid adiabatic calorimeter: 1) casing (shell) of calorimeter, 2) calorimetric vessel, 3) platinum resistance thermometers, 4) heater, 5) calorimetric bomb, 6) mixers, 7) driving magnet of mixers.

makes it possible to reduce errors induced by heat transfer. Any temperature variation in the calorimetric vessel due to the release of heat of combustion is accompanied by heating of the liquid in the thermostatic shell. Water or an electrolyte (potassium hydroxide) solution heated by an electric current are usually used as a thermostabilizing liquid. Only two temperature measurements in the calorinetric vessel are required in an ideal adiabatic CC: before the ignition of the sample and upon completion of the heat transfer between the CB and water. Actual constructions of adiabatic CCs do require corrections for heat transfer. Figure 3 presents a diagram of the OQ-203 liquid adiabatic calorimeter (Hungary) (Table 1, item 7). The CB is situated within the internal calorimetric vessel 2 filled with water, which is hermetically sealed by an upper cover. External casing (shell) 1 is also filled with water. Platinum resistance thermometers are situated in the calorimetric vessel and the shell, and an electric heater and channels for water cooling are situated within the shell. To improve heat transfer, magnetically-driven mixers are situated in the calorimetric vessel and the shell. The adiabatic operation mode of the calorimeter is provided by integrated circuit-based electronic devices. A thyristor-based controller maintains the temperature of the shell at a value practically equal to that of the calorimetric vessel by controlling the systems of electric heating and water cooling. The power of the shell heating can be as high as 2 kW, the sensitivity of the sensor and control system is not worse than 0.01 K, and the temperature difference between the casing and calorimetric vessel does not exceed 0.05 K.

Janke & Kunkel GmbH (Germany) produce the IKA-C400 calorimetric system (Table 1, item 8) for determination of the heat of combustion of solid and liquid substances (coal, oils, food products, etc.). The device is automated and meets the requirements of the FRG and the American Society for Testing Materials. The system includes, in addition to the calorimeter itself, a DKT 400 digital thermometer, a KV 400 water cooler, and a controller with an SRD 100 recording system.

It should be noted that a number of calorimeters can operate in both isoperibolic and adiabatic modes. In this case, in order to achieve the required accuracy of SHC measurements, corrections for heat transfer should be evaluated with the corresponding errors, and the necessary accuracy of adjusting the shell temperature control should be provided. In a calibrating CC developed at the D. I. Mendeleev All-Russian Scientific Research Institute of Mechanical Engineering (St. Petersburg, Russia), in order to provide measurements with an error of 0.01-0.03%, the error in evaluation of the correction for the heat transfer should not exceed 0.0001 K, and fluctuations in the temperature of the shell should not exceed 0.003 K [21].

The calorimeters described above, both isoperibolic and adiabatic, require weighing of the calorimetric liquid before each measurement. There are also other pitfalls inherent in liquid CCs: evaporation of water, heat release due to friction in bearings of the mixer, and heat transfer in mixers. Massive CCs, where metals with a high thermal conductivity are used, are free of these pitfalls.

Massive CCs [3, 9]. As opposed to liquid CCs, where the heat released in the bomb propagates rapidly along the calorimetric vessel owing to the convective heat transfer stimulated by the mixer, massive CCs utilize conductive heat transfer. The rate of thermal equilibration depends on the thermal conductivity of the material of the unit, its density, and the quality of the thermal contact of the bomb with the unit. The assumption of the simplified theory [2] of massive calorimeters that temperature gradients are absent in the calorimetric system during the experiment is, as a rule, incorrect, and therefore one should try to achieve reproducibility of the temperature field during calibration and in experiments [9]. The design of massive CC should ensure a fast and uniform distribution of the heat flow in the calorimetric system and exact reproducibility of the positions of all parts of the system in each experiment.

A description of the Euken–Meyer calorimeter, which was among the first massive CCs, is presented in [3]. Small amounts of a substance (30-40 mg) are burnt in an oxygen atmosphere in a closed copper vessel with a volume of 250 cm^3 at atmospheric pressure. This reaction vessel is simultaneously the calorimetric substance and CB. A slot for a mercury thermometer is situated in its body. The vessel is hung on a steel wire within a thermoinsulating cylindrical shield of polished copper foil. The shell consists of a double-walled copper vessel filled with water (thermostat). To achieve complete and uniform combustion of the substance under investigation, e.g. coal, it is mixed with an inert powder (20–30% magnesium oxide).

Gentry Instruments (USA) proposes a low-capacity CC for investigation of small amounts of substances. A miniature CB is situated on an aluminum ring support, whose temperature is measured by 16 copper-constantan thermocouples. A concave metallic shield protects the system from convection. The reproducibility of measurements with benzoic acid used as a reference substance is 2%. This CC is a massive calorimeter with the CB maintained in thermal contact with the calorimetric substance, i.e., the bomb support [3].

An adiabatic massive CC has been developed at the All-Russian Scientific Research Institute of Mechanical Engineering for carrying out metrological experiments [9]. The setup consists of a massive CC with a device for temperature measurements, a unit for maintaining and controlling temperature conditions of operation of the calorimeter, a setup for evaluation of the thermal equivalent of the calorimeter (electric calibration), vacuum equipment, and service equipment (systems for oxygen purification, analysis of combustion products, titration of the bomb liquid, a press for briquetting the substance under investigation, and devices for setting up and measuring the energy of sample ignition).

The design of the calorimeter makes it possible to carry out experiments with both an isothermal shell (upon evacuation of the air space) and an adabatic one. The calorimeter consists of a bomb and a massive calorimetric unit fabricated in the form of spherical bodies. The CB is made of stainless steel in the form of a one-piece sphere 98 mm in diameter. A neck hermetically sealed with a self-sealing bushing is situated in the upper portion of the CB. A calibrated electric heater is placed in a groove threaded on the surface of the CB. A chambered edge of the CB is inserted into the 16-kg massive block. With this weight, the total temperature rise of the calorimetric system upon combustion of a 0.5-g sample of benzoic acid is about 2 K. The massive unit has a technological slit in its transverse cross-section, which divides it into two symmetric parts. Both parts of the massive unit are joined along the fitted surface by three pins. A conic opening sealed by a cap with a fitted conic surface is situated in the upper part of the massive unit. The calorimetric system is placed in a spherical brass shell. Two spherical screens are concentrically placed between the calorimetric system and the shell. The internal screen is adiabatic due to a heater situated in the screen, which makes it possible to maintain its temperature corresponding to heating of the massive unit. The brass shell of the CC is placed in a liquid thermostat, where the temperature of water is maintained at the necessary level with an error not exceeding 0.001 K.

Platinum resistance thermometers and thermocouples are used as temperature sensors. A resistance thermometer situated on the massive unit makes it possible to determine the integral temperature of the surface of the calorimetric system with an error not exceeding 0.0001 K, which is necessary for evaluation of the correction

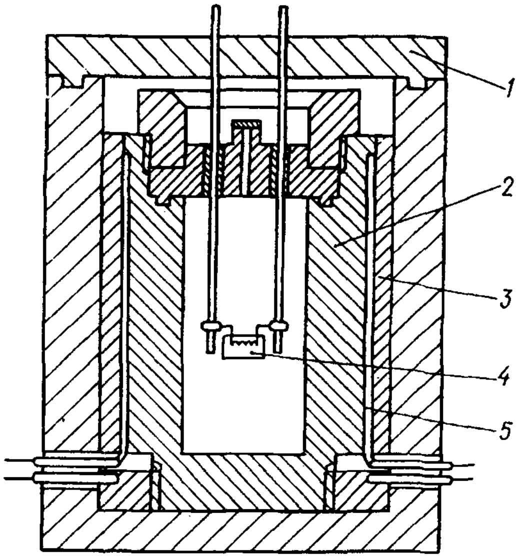

Fig. 4. Massive calorimeter with thermoinsulating shell: 1) thermoinsulating shell, 2) CB, 3) copper cylinder, 4) fuel sample, 5) sensors.

for the heat transfer from the system to the environment. The temperature difference between the calorimetric system and adiabatic screen is monitored by two resistance thermometers connected to a differential bridge circuit and placed on the surface of the massive unit and on the inner surface of the adiabatic screen. The temperature difference between the adiabatic and background screens is monitored by a differential copper-constantan thermocouple with ten junctions.

The massive calorimeter is calibrated by both the absolute method against the electric heating power and the reference method, i.e., by combustion of a reference substance, K-1 brand benzoic acid, in the calorimeter. At a confidence level 0.95 the root-mean-square deviation of the thermal equivalent is 0.02%.

The above-described calorimeter and other CCs developed at the All-Russia Scientific Research Institute of Mechanical Engineering provide a high accuracy of measurements [2, 7, 21] and are used as calibrating instruments in an aptitude test scheme for measuring of the heat of combustion [5]. However, they are practically unsuitable for large-scale measurements due to the complexity of construction elements, duration of the preparation for the experiment, and their expensiveness.

In Ukraine, a national system for the quality control of fuel with respect to the heat of combustion is presently being developed, which includes the State Check Test Scheme, primary standard [22], and working means of measurement of the heat of combustion [20].

Massive CCs with a Thermoinsulating Shell. They are developed by foreign companies and are commercially available. In these devices, instead of isothermic or adiabatic shells, a high-efficiency thermal insulation is used. These CCs occupy an intermediate place between isoperibolic and ideal adiabatic devices, since they have heat losses through the insulation, and corrections for the heat transfer should be taken into account.

A scheme of a calorimeter patented in Great Britain [23] is presented in Fig. 4. The cylindrical CB of stainless steel and embracing copper cylinder form the kernel of the calorimetric system, which is placed in a thermoinsulating shell. A change in the temperature induced by the combustion of the fuel sample is measured by sensors (primary temperature transformers) placed between the bomb surface and copper cylinder that equalizes the temperature field of the calorimetric system. The proposed method of sensor placing makes it possible to minimize the thermal drift of the calorimeter. After measurements, the CB is cooled by a Peltier cooler brought in thermal contact with the bomb upon its withdrawal from the CC.

Devices developed according to the principle described are easily automated. They can be used in quick measurements of the SHC. Thus, Janke & Kunkel GmbH propose the IKA C700T System (Table 1, item 9), where the temperature is measured by gage probes built into the CB. A microprocessor calculates temperature corrections for the heat transfer by the Regnault–Pfaundler method [2], and then evaluates the SHC value. The equipment

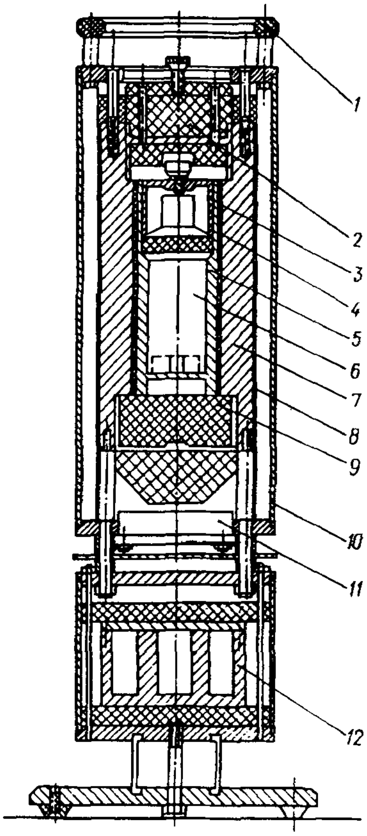

Fig. 5. KTS-2 conductive isoperibolic calorimerter: 1) ring handle, 2) upper cover, 3) cover of cell, 4) thermometric shell (THF), 5) cylinder of calorimetric cell, 6) CB, 7) body, 8) heater, 9) thermoinsulating bushing, 10) casing, 11) ventilator, 12) department of electronic units.

supplied by the company includes the following devices: calorimeter with a high-quality thermoinsulation (C700), calorimetric bomb with electronic sensors for temperature measurements (C710), thermoelectric bomb cooler (C701), device for filling bombs with oxygen (C702), interface and microprocessor for expansion of the spectrum of applications by connecting electronic weighing machine, computer interface, etc. (C703), and printer for the printout of experimental transactions.

The C700T system provides a high efficiency when performing large-scale technical measurements of the SHC. According to the catalog of Janke & Kunkel GmbH [19], with the three interchangeable CBs used, the C700T system makes it possible to carry out up to 196 SHC measurements per eight-hour shift. Unfortunately, information on the guaranteed accuracy of measurements is not provided in the catalog.

Isoperibolic Conductive Calorimeters. All the above-described devices operate according to the enthalpy principle and are in fact integrating calorimeters, since the measured output signal (increase in temperature) is proportional to the total heat released in combustion from beginning to end. However, devices in which the output signal is proportional to the heat released in the calorimetric cell are widely used. These devices can be considered "oscilloscope" calorimeters. The heat released in the calorimetric cell is drawn aisde to the isothermic shell due to conductive heat transfer, and the heat flux from the calorimetric cell to the shell is continuously measured. The total amount of heat released in the process under investigation can be determined by integrating the output signal of the calorimeter by secondary gage equipment.

Conductive calorimeters developed by Tian and improved by Kalwe [24] include a calorimetric cell surrounded by a multijunction thermoelectric pile and placed in a temperature-controlled body. In these devices, the total heat release can be determined not only by integrating the heat flux but also by the ballistic method, i.e., from the maximum value of the signal from the thermoelectric pile. Presently, Tian–Kalwe calorimeters are widely used in various thermophysical, thermochemical, and biological investigations [3, 25]. These devices are microcalorimeters for investigation of processes with a small heat release in relatively small volumes. In the known conductive heat flux calorimeters, the volume of the calorimetric cell does not exceed, as a rule, 100 cm^3, and the maximum heat release power is 8–10 W at the total heat release energy up to 1 kJ.

Investigations on the automation of the process of calorimetric measurements have been carried out at the Institute of Chemical Physics of the Russian Academy of Sciences, and a series of methods for accelerated measurements of the combustion energy has been proposed. The AKS-3M automated calorimeter used for measurements of the heat of combustion of various substances has been developed [26].

Model CCs utilizing the principle of the isoperibolic conductive calorimeter have been developed and are produced in small lots at the Institute for Problems of Energy Saving of the National Academy of Sciences of Ukraine in cooperation with the "Shtorm" Development Department at the National Technical University. The KTS-1 and KTS-2 calorimeters are designed for measurements of the SHC of various types of fuels, are automated, easy in operation, do not require a special laboratory room with stable temperature conditions, are less influenced by operator's personal equations compared to liquid calorimeters. The thermal unit of KTS-type calorimeters (Fig. 5) contains a duraluminum calorimetric cell where a standard CB of stainless steel is placed. The flat surfaces of the calorimetric cell and the entire cylindrical thermal block are insulated from the environment by a high-efficiency thermal insulation, and the lateral cylindrical surface of the calorimetric cell has a thermometric shell, which is a primary measuring thermoelectric transformer of heat flux (THF) of the generator type. The THF is manufactured in the form of a cylindrical wall and consists of more than 70,000 galvanic elements and makes it possible to measure heat flux with high sensitivity. The outer surface of the THF is in contact with the inner one of a massive cylindrical body of duraluminum with an electric heater and resistance thermometer situated on its outer surface, which are used for thermal stabilization of the surface of the thermal unit. The KTS-2 model differs from the KTS-1 model [26] by a series of design solutions aimed at decreasing the duration of the preparation and measurement, and stabilizing temperature regimes of operation. An auxiliary electric heater used for establishing the initial temperature regime during preparation of the device for measurements, is situated in between the inner THF surface and calorimetric cell. The removal of excess thermal energy from the surface of the body is carried out by an air flow generated by a built-in fan in a ring-shaped gap between the body and the protective metal case. A temperature-stabilized compartment for an amplifier of the THF signal and electronic system for temperature stabilization is provided in the thermal unit. A separate electronics unit is included in the KTS-2 calorimeter, which contains a system for ignition of the fuel sample, and gage and signal processing systems. The gage and signal processing system is developed on the basis of a single-chip microprocessor and automatically carries out measurements of the HTF signal, its integration during the operation mode, and monitors results of measurements of the heat of combustion of a sample in digital form on a display.

The preparation to measurements with KTS-type devices is carried out in the same manner as in the case of other bomb calorimeters: a fuel sample is weighed and placed in the CB, which is then filled with oxygen. Then the CB is placed in the calorimetric cell, the fuel ignition wires are connected, and the covers of the cell and the thermal unit are closed. Upon heating of the CB to the temperature of stabilization of the thermal unit and establishing a stationary regime, an operator ignites a fuel sample by pressing a button. The microprocessor starts to acquire and process the HTF signal. After the ignition of the fuel, the HTF signal grows sharply and in 1.5–2.0 min reaches its maximum value, and then starts to decrease slowly. Approximately an hour after the ignition of the fuel sample the thermal unit again reaches a stationary regime. The heat released in the CB during the combustion of the fuel sample is calculated by the microprocessor simultaneously by two methods: ballistic and integral. In the ballistic method, the heat released is calculated from the value of the maximum HTF signal and the result can be obtained in 3–4 min after the ignition of the fuel.

In the integral method, the total heat released Q_{tot} is calculated from the value of the HTF signal integrated over one hour after the ignition by the formula

$$Q_{tot} = K_c \int_{\tau_{start}}^{\tau_{end}} (E_{HTF} - E_{start})\, d\tau ,$$

where $\tau_{end} - \tau_{start} = 1$ h.

Experimental models of the KTS-1 calorimeter passed the State Metrological Certification at the Ukrainian Center for Standardization, Metrology, and Certification and were permitted as working means of measurements of the heat of combustion of fuel with a 0.2 accuracy grade. Calorimeters of the KTS-2 model with improved operation characteristics are presently passing tests. KTS-type calorimeters can become a basic working means in the Ukrainian National System of fuel quality control.

The analysis of design types and technical characteristics of bomb CCs developed in recent years makes it possible to reveal two main trends in the development of these devices. First, a high automation level of measurements and data processing implemented on the basis of the microprocessor techniques and high-accuracy primary transformers of the temperature and heat flux is characteristic of modern CCs. Second, the development of dry (water-free) CCs, where constructions with stable thermophysical parameters and high-efficiency thermoinsulators are used, is noteworthy. Normalized metrological characteristics of bomb CCs of various types meet modern industrial requirements and are virtually limiting for working means of measurements [14]. However, the use of automated dry devices makes it possible to facilitate the operator's job, reduce requirements to his/her qualification, and decrease substantially the probability of subjective equations during measurements.

NOTATION

q, specific heat of combustion of fuel; q_1, specific heat of combustion of ignition wire; K, effective heat content (thermal equivalent) of calorimeter; t_{start} and t_{end}, initial and final temperatures of the main period expressed in divisions of the thermometer scale; h_{start} and h_{end}, corrections for thermometer readings at temperatures t_{start} and t_{end}, respectively; Δt, correction for heat transfer from calorimetric vessel to shell expressed in divisions of the scale; G_1, mass of wire for ignition; G, mass of fuel sample; H, value of the thermometer scale division in degrees; V_1, average change of temperature for 30 sec during the initial period; V_2, average change of temperature for 30 sec in the final period; b, number of half-minute divisions of the main period with the fast rise of temperature (0.3 K and higher); r, number of half-minute divisions of the main period not accounted for in the quantity b; K_c, calibrating coefficient; E_{HTF}, HTF signal; τ_{start} and τ_{end}, initial (fuel ignition) and final instants; E_{start}, value of HTF signal at the instant τ_{start}.

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