MEASUREMENT OF HEAT OF HYDRATION OF HYDRAULIC CEMENTITIOUS MATERIALS USING ISOTHERMAL CONDUCTION CALORIMETRY
(Kansas Test Method KTMR-38)

1. SCOPE

1.1. This test method specifies the apparatus and procedure for determining total heat of hydration of hydraulic cementitious materials at test ages up to 7 days by isothermal conduction calorimetry. **KTMR-38** reflects testing procedures found in **ASTM C1702** and the KDOT Operator's Manual for Isothermal Calorimetry using the TAM Air Calorimeter.

1.2. This test method also outputs data on rate of heat of hydration versus time that is useful for other analytical purposes, as covered in **ASTM C1679**.

2. REFERENCED DOCUMENTS

2.1 ASTM C 511; Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms and Water Storage Tanks Used in the Testing of hydraulic Cements and Concretes

2.2. ASTM C1679; Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry

2.3. ASTM C1702; Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry

2.4. KDOT Operator's Manual for Isothermal Calorimetry using the TAM Air Calorimeter

3. APPARATUS

3.1 Balance—Accurate to 0.01 g.

3.2. Volumetric Dispenser—A device for measuring volume or mass of water, accurate to 0.1 mL. This could be a syringe, pipette, or weighing device.
Note: 10 μL and 50 μL micro-syringes and a 2500 μL auto-pipette have been found to work well for measuring liquid admixtures and mixing water, respectively.

3.3. Sample Holder—A device that holds the cement paste and provides intimate contact with the calorimeter heat sensing device and prevents evaporation of mixing water. If using commercially manufactured equipment, consult the recommendations of the manufacturer in choosing sample holders.
Note 1: The plastic sample vials designed for use with the TAM Air calorimeter meet these requirements.

3.4. Reference Specimen—A sample fabricated from an inert material with similar heat capacity and shape as the test sample. The reference specimen is used in the reference cell. The thermal mass of the inert reference specimens should always be similar to the target cement paste. Calculations for determining the thermal mass of reference specimens are given in the KDOT Operator's Manual for Isothermal Calorimetry using the TAM Air Calorimeter.

3.5. Isothermal Calorimeter—The calorimeter shall consist of a sample holder for the test and reference specimens, each thermally connected to heat-flow sensors, which are thermally connected to a constant temperature heat sink. The actual design of an individual instrument, whether commercial or homemade,

may vary, but it should follow the criteria given in **ASTM C1702** for instrument stability, instrument sensitivity, isothermal conditions and data acquisition equipment.
Note 2: The TAM Air calorimeter manufactured by TA Instruments meets the requirements of section 3.5.

3.6. Vortex Mixer—The mixing device shall be a bench-top vortex-type mixer, as commonly used for mixing ingredients in test tubes. Note: the Thermo Scientific Vortex Maxi Mix I meets these requirements.

4. INSTRUMENT CALIBRATION

4.1. Calibrate the calorimeter as described in **ASTM C1702** or according to instrument specific calibration procedures provided by the calorimeter manufacturer.

5. CONDITIONING

5.1. Maintain the temperature of the room with the calorimeter at not less than 20°C and not more than 30°C. The temperature of the room should not vary by more than 1°C. The relative humidity should be less than 65%.
Note: A cement mixing room that meets the requirements in **ASTM C511** will maintain a temperature of 23.0 ± 4.0 °C.

5.2. Maintain the operating temperature of the calorimeter at 23 °C. Verify the temperature setting at least 18 hours before starting the test.

5.3. Allow the cementitious materials, mixing water and reference specimens to come to thermal equilibrium at 23 °C before starting a calorimeter test.

5.3.1. Place reference specimens and closed sample vials with adequate mixing water for the samples to be tested in the calorimeter at least 12 hours before starting the test. Put the reference samples in the reference side of the calorimeter channel that will be used for testing. Place the mixing water vials in a channel that will not be used for testing.

5.3.2. Weigh the dry cementitious materials to the nearest 0.01 g and place into the sample vial. Take care not to spill any material on the neck or over the outer wall of the vial. Close the sample vial and place in the sample side of the channel that will be used for testing at least three hours before starting the test.

6. TEST PROCEDURE

6.1. Start the calorimeter software and enter testing information and sample data as described in the KDOT Operator's Manual for Isothermal Calorimetry using the TAM Air Calorimeter. Use a new experiment for each sample that will be tested.

6.1.1. The data will be normalized using the mass of the cement.

6.1.2. Run a 30-minute initial baseline to verify the thermal stability of the calorimeter.

6.2. Start sample preparation and mixing.

6.2.1. Wear gloves while preparing and mixing samples to minimize heat transfer to the specimens.

6.2.2. Measure the liquid admixtures (if any) to the nearest μL using a micro-liter syringe.

6.2.3. Remove the mixing water vials from the calorimeter.

6.2.4. Start a 30-minute baseline measurement

6.2.5. After the baseline measurement has completed, remove the test sample vial and the reference specimen containing the cementitious materials from one channel of the calorimeter. Hold the reference specimen whenever the test sample vial is held during sample preparation to equalize the heat flows in the two vials. Close the calorimeter as soon as possible after opening.

6.2.6. Blend the dry cementitious material in the test sample vial on the vortex mixer for 5-7 seconds.

6.2.7. Tap the bottom of the test sample vial firmly. Tap the lid firmly 5-10 times to settle the cementitious powder at the bottom of the vial.

6.2.8. Use the auto-pipette to add water from the conditioned water vial to the test sample vial.

6.2.9. Mark the time the water was added.

6.2.10. Cap the sample vial and mix on the vortex mixer for 30 seconds. Hold the sample vial at a slight angle on the mixer and turn it occasionally to get good mixing action.

6.2.11. Tap the test sample vial on the counter and tap the top again to settle the paste in the bottom of the vial.

6.2.12. If liquid admixtures are to be used, use the micro-liter syringe or equivalent to drop the admixtures on the surface of cement-water paste in the test sample vial. Do not touch syringe tip to surface. Recap test sample vial.

6.2.13. Mix for another 30 seconds on the vortex mixer. Tap the vial on the counter and tap the top again to settle the paste in the bottom of the vial to ensure the paste is level in the bottom of the vial and large amounts do not remain on the walls near the top.

6.2.14. Clean the outer surface of the ampoule with a new, dry, dust-free paper tissue.

6.2.15. Insert the test sample vial and the reference specimen into the calorimeter. Close the calorimeter as soon as possible after opening.

6.2.16. Immediately on inserting the vials, record the hour, minute and second of the time inserted.

6.3. Allow the calorimeter test to run for at least 48 hours. Disturb the calorimeter as little as possible while tests are in progress.

6.4. Once all calorimeter tests are complete, end all of the individual experiments that are running before opening the calorimeter to remove any samples.

6.4.1. An ending baseline measurement is not necessary for calorimeter tests lasting less than seven days.

6. THERMAL MASS CALCULATIONS

6.1. The thermal mass of a given material is calculated by multiplying the mass by the specific heat capacity of the material. The thermal mass of each component is added to determine the total thermal mass of a mixture. The thermal mass of the reference sample and the analyzed sample should match within 20%. Specific heat capacities of common concrete-making materials are given in Table 1.
Example: A paste sample has 5 g of cement and 10 g of water. The thermal mass of the sample is:
$5\ g \times (0.75\ J/(g \cdot K)) + 10\ g \times (4.18\ J/(g \cdot K)) = 3.75\ J/K + 41.8\ J/K = 45.55\ J/K$

Table 1. Specific heat capacities of materials used in concrete

Material	**Specific heat capacity, J/(g·K)**
Portland cement	0.75
Water	4.18
Fly ash and slag	0.80
Quartz sand	0.75
Limestone	0.84