FLAME EXTINGUISHING CONCENTRATION BY THE CUP BURNER METHOD: INERT GAS THEORY, PERFORMANCE & ADVANCING THE METHOD

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ABSTRACT

The determination of flame extinguishing concentration of a gaseous agent for a particular class of flame (for example for liquid, solid or plastic fuels) is the basis from which a minimum "design" concentration of gaseous agent is determined by contemporary standards relating to gaseous fire extinguishing systems. In the case of Class B fuels, flammable liquids, both a laboratory test, the cup burner method, and large scale tests have been specified by standards as the basis of establishing extinguishing concentration. While the general requirements for conducting the various extinguishing tests are specified in standards, it is observed that there are frequently material inconsistencies in the test specifications, the results reported by various parties, or both. The cup burner method, in particular, has great value due to its conceptual simplicity and low cost. Cup burner data was submitted by several parties in 2002 to ISO TC 21/SC 8*. The data appeared to exhibit significant inconsistencies, particularly for inert gases. Inasmuch as important safety design decisions and competitive positions are affected by these data it is important that the test method be well specified and have high reproducibility among laboratories.

This paper focuses on five inert gas fire extinguishing agents, four of which are in commercial use as alternatives to halon 1301 in total flooding applications, with a review of cup burner extinguishing data as appears in several publications and regulatory standards, development of the theory of inert gas extinguishing, presentation of a new and coherent set of extinguishing data, and comparison results with predicted values. The new data set validates the theory, demonstrates repeatability, and supports the need to make enhancements in the cup burner method that will lead to improved inter-laboratory reproducibility.

* Data was provided as part of the current revision cycle in revising ISO 14520 "Gaseous fire extinguishing systems – physical properties and system design." Since ISO 14520 is in revision the data submitted should be considered to be preliminary and subject to change.

INTRODUCTION

Fundamental to the use of gaseous fire extinguishing agents in total flooding fire suppression systems is the notion that there exists a lowest concentration of the agent which when present in air renders the "inhibited" air incapable of supporting diffusion flame combustion. The limiting concentration is referred to as the minimum extinguishing concentration, or MEC. The value of the MEC will be dependent on several variables including the properties of the fuel and agent and fluid mechanical details at the attachment point of the flame to its stabilizing substrate. The method for establishing the MEC value is given in national and international standards such as NFPA 2001 [1], AS 4214 [2] and ISO 14502 [3]. In the case of Class B (flammable liquid) fuels the cup burner method has assumed a prominent position as the definitive method for measuring MEC. NFPA 2001 Section 3-4.2.1 requires that "The flame extinguishing concentration for Class B fuels shall be determined by the cup burner method …." AS 4214 Section 3.4.2.3 requires that "The minimum design concentration for Class B fuels for each extinguishing agent shall be the cup burner fire extinguishing concentration for each Class B fuel plus a safety factor of 30%." ISO 14520 Section 7.5.1.2 requires that "The extinguishing concentration used shall be that demonstrated by the cup burner test …". The Class B MEC value is multiplied by a design factor (often referred to as the *safety factor*) of 1.3 to determine the minimum design concentration of the inert gas agent for commercial fire protection system applications. The responsibility for establishing the recognized value of the cup burner MEC usually falls to the manufacturer of the agent in question. The cup burner MEC value also found a role in third party approvals procedures. In obtaining third-party (e.g., UL or FM) approval of a fixed gaseous fire extinguishing system it is usually necessary to perform large-scale tests including, in the case of Class B fuels, pan fire tests. Underwriters Laboratories approvals standards [4] interpret pan fire test results in relation to the accepted cup burner value of the test fuel which is usually commercial heptane, a blend of C_7 alkanes.

The cup burner method, which had its origins as a research tool [5], has evolved as the method for establishing the design criteria for commercial fire suppression systems. The accuracy of the method is important in setting the MEC and the consequent design concentration. The statistical reproducibility of results obtained by the cup burner method, as determined from lab to lab, has never been established. That is, a competent laboratory may produce results that are different for the same fuel-agent combination, or which are otherwise inconsistent with results from other laboratories. In fact, examination of inert gas MEC values that today form the basis of fire protection system designs shows small but significant inconsistencies to the point that the rank ordering of inert gas MECs according to established physical principles is not correct. If the MEC as determined by the cup burner method is the basis of establishing both safe design and commercial positions in the marketplace, it would appear that resolution of the inconsistent aspects of the method is in the interest of all parties. The objectives of the work presented in this paper are (a) derivation of an expression for the extinguishing concentrations of inert gases in relation to the operative parameters which are the heat capacity of the inert gas agent, properties of the fuel, and the effective limiting combustion temperature, (b) development of a self-consistent set of cup burner extinguishing data, and (c) proposal of approaches for advancing the cup burner method that would help improve its fundamental inter-laboratory reproducibility.

INCONSISTENCIES IN CUP BURNER EXTINGUISHING CONCENTRATION VALUES

The mechanism of flame extinguishment by inert gases has been clearly established on theoretical and experimental grounds as being rooted in the heat capacity of the inert gas agent, though the light monatomic gases (helium and neon) exhibit thermal conductivity effects. (A derivation of the heat capacity effect in somewhat different form from that of Sheinson et al [7] and Saito et al [9] is given later.) As such, the simple rank ordering of inert gas extinguishing concentration should be in the order of agent heat capacity. The cup burner values, for n-heptane fuel, as cited in current and draft fire protection system standards are given in Table 1. The ordering of the agents in Table 1 are in descending order of the agent heat capacity, given in the third column. The cup burner values, if consistently determined, should decrease uniformly with increasing heat capacity value of the agent. As is evident, this is not the case. The extinguishing concentration value for each agent in Table 1 was reported by a different laboratory. Determinations reported to the different standards were generally made at different times.

Table 1. Cup Burner Values in Regulatory Use, Vol. %; Fuel: n-Heptane

Agent	Composition, mol %	Cp, J/mol-K	NFPA 2001	AS 4214	ISO 14520	ISO TC 21 SC/8 [6]
IG-01	Argon: 100%	20.8	42	-	37.5	39.2
IG-55	N_2/Ar : 50/50	24.6	35	32.3	32.3	36.5
IG-541	N_2/Ar/CO_2: 52/40/8	26.1	31	33.8	33.8	31.7
IG-100	Nitrogen: 100%	28.5	31	-	33.6	33.6

Table 2 contains cup burner data as reported by various authors. This table has the virtue of reporting results for multiple agents from the same laboratory, thus introducing a degree of measurement consistency. With one exception, the ordering of cup burner values with heat capacity is preserved, though inter-laboratory variation for a given agent is as much as 14% pointing to a lack of lab-to-lab reproducibility in the method.

Table 2. Literature Cup Burner Values, Vol. %; Fuel: n-heptane

Agent	Composition, mol %	Cp, J/mol-K	Hirst & Booth	Sheinson et al. [7]	Dlugo-gorski et al. [8]	Saito et al. [9]	Moore et al. [10]
IG-01	Argon: 100%	20.8	-	41	39	43.3	38
IG-55	N_2/Ar : 50/50	24.6	-	-	-	-	28
IG-541	N_2/Ar/CO_2: 52/40/8	26.1	-	-	32	35.6	-
IG-100	Nitrogen: 100%	28.5	30.2	30	29	33.6	30
IG-505	N_2/CO_2 : 50/50*	33.0	-	-	-	25.9	-
CO_2	CO_2: 100%	37.5	20.5	21	-	22	20.4

* This gas mixture is not in commercial use as a total flood fire extinguishing agent.

THERMOCHEMISTRY AND EXTINCTION BY INERT GAS ADDITION

Consider the reaction, at atmospheric pressure and 298 K, of one mole of an aliphatic hydrocarbon fuel with a stoichiometric amount of air to yield the products CO_2 and H_2O.

$$C_nH_{2n+2} + \frac{3n+1}{2}\{O_2 + 3.76N_2\} \rightarrow nCO_2 + (n+1)H_2O + 1.88(3n+1)N_2 \qquad (1)$$

The heat of combustion, Q, per mole of the fuel species in a reaction involving K components is given by [11]

$$Q = -\Delta h^o_{r,298} = -\sum_{k=1}^{K} \nu_k h^o_{k,298} \quad \text{(since Q is a positive number)} \qquad (2)$$

In the case of an adiabatic process the enthalpy is conserved leading to a flame temperature, T_f, which satisfies

$$Q = \sum_{i=1}^{P} \nu_i \int_{298}^{T_f} C_i dT \qquad (3)$$

where the sum is over the product species, *i to P*. The equilibrium products at T_f, which for aliphatic hydrocarbons is typically about 2200 K [12], include small amounts of minor species such as CO, O, H_2, OH, H, and others not material to the present discussion.

The addition of an inert gas species to a mixture of fuel and air has the effect of lowering the flame temperature owing to the fact that the heat of reaction must be distributed over more mass. When the concentration of the added inert gas, X_G, is large enough and the corresponding flame temperature, T_f, low enough the extinction temperature, $T_{e,}$ is reached at which propagation just fails. The energy balance for adiabatic combustion at the extinction temperature is

$$Q = \sum_{i=1}^{P} \nu_i \int_{298}^{T_e} C_i dT + \sum_{j=1}^{G} \nu_j \int_{298}^{T_e} C_j dT \tag{4}$$

The first term on the right of (4) is the heat absorbed by the normal combustion products, P, to reach $T_{e.}$ The second term on the right is the heat absorbed by the added inert gas extinguishing agent, G, which may be multi-component. Heat which may be lost to the surroundings (by radiation or conduction) is represented below by q. Below it is shown that q appears to be small enough to neglect but it will be retained in the analysis for the present. The heat balance of (4) is more fully represented as

$$Q = \sum_{i=1}^{P} \nu_i \int_{298}^{T_e} C_i dT + \sum_{j=1}^{G} \nu_j \int_{298}^{T_e} C_j dT + q \tag{5}$$

The integration of the heat capacity over the temperature range 298 K to T_e is, ΔH_P or ΔH_G, the enthalpy change per mole of normal combustion products and added inert gas agent, respectively. The total enthalpy change for the normal combustion products is ΔH_P (kJ/mol fuel). The enthalpy change of the added inert gas agent is $\nu_G \Delta h_G$ (kJ/mol fuel) where ν_G is the quantity of added inert gas (moles/ mole fuel) and Δh_G is the enthalpy change per mole between 298 K and T_e. With this, Eq. 5 can be reorganized to solve for ν_G, the total quantity of added inert gas as shown in Eq. 6.

$$\nu_G = \frac{Q - \Delta H_P - q}{\Delta h_G} \tag{6}$$

For a given fuel type, extinction temperature (T_e), and flame characteristic (q) the quantity of inert gas extinguishing agent, per mole of fuel, is inversely related to ΔH_G , or the integrated agent heat capacity . In assessing agent performance in diffusion flame extinction the parameter of interest is the mole fraction of the added inert gas in the air-agent mixture which is given by

$$X_G = \frac{\nu_G}{\nu_{Air} + \nu_G} \tag{7}$$

(In the case of premixed combustion the denominator of (7) is increased by *1* to include the one mole of fuel.) The specification of ν_{Air} derives from the reaction (1). For an aliphatic hydrocarbon fuel Eq. 7 becomes

$$X_G = \frac{\nu_G}{\frac{3n+1}{2} 4.76 + \nu_G} \quad \text{or} \quad X_G = \frac{\nu_G}{7.14n + 2.38 + \nu_G} \tag{8}$$

In terms of the system properties the extinguishing concentration of an added inert gas has the form

$$X_G = \frac{\dfrac{Q - \Delta H_P - q}{\Delta h_G}}{7.14n + 2.38 + \dfrac{Q - \Delta H_P - q}{\Delta h_G}} \tag{9}$$

The inert gas extinguishing concentration for a given fuel and flame type is, therefore, a function of the stoichiometry (n), effective extinguishing temperature (T_e), and the heat capacity of the added inert gas (C),

$$X_G = X_G(n,\ T_e\ ,C)\ . \tag{10}$$

The result shown in Eq. 9 is similar to that obtained by Saito et al and by Sheinson et al.

Estimation of q. It is observed from data for the stoichiometric hexane-air system with added nitrogen [13] that the extinction limit is reached when nitrogen added amounts to 21.3 mol N_2/mol fuel, or 31.5% of the mixture. The corresponding extinction temperature was calculated as 1853 K [14]. Equation (6) was used to solve for q (where Q = 3,888 kJ/mol; ΔH (1853-298): N_2 = 50.724; CO_2 = 82.593; H_2O = 65.342 kJ/mol) to obtain a value of 43.6 kJ/mol fuel, ~1% of Q, which is probably less than the accuracy of this calculation. Thus, q is taken to be nil for the pre-mixed case.

"ICI" CUP BURNER AND DIFFUSION FLAME EXTINCTION

The essential elements of the cup burner, illustrated in Annex A, are the cup and chimney. Means to measure and control gas flows, diffuse the inlet air flow at the base of the chimney and to control the fuel liquid level are also important. The sensitivity of the extinguishing concentration result to scale effects has been studied by Saso et al [15]. One test variable is air flow rate which has somewhat differing effects depending on whether the added agent is an inert gas or a halogenated compound. Most work is reported for air flow rates in the range of 20 to 50 l/min (6 to 15 cm/s nominal velocity based on an 85 mm I.D. chimney) with 30 or 40 l/min being most common. The ISO TC 21/SC 8 committee on *Gaseous Media and Fixed Fire-Extinguishing Systems Using Gas* has elected to accept data based on 40 l/min air flow rate only. Pre-burn time is important as it affects the temperature of the fuel and the cup itself. The cup burner used in this work was originally acquired from Imperial Chemicals Industries (ICI Mond Division, once a major producer of halons and where Hirst and Booth did their seminal work on the cup burner) in the mid 1970's. The dimensions of the ICI cup burner have served as the benchmark for what is today referred to as the standard apparatus as described in NFPA 2001 and ISO 14520.

The determinations of extinguishing concentration for three inert gases and two blends using the ICI cup burner are given in Table 3.

Table 3. Predicted and Measured Cup Burner Values; Fuel: n-Heptane

Agent	C(298K) J/mol-K	Δh_G * kJ/mol	Predicted Vol. %	Measured Vol. %	Test Date
Argon	20.8	32.693	42.4%	43.2%**	2/20/03
				42.3%	10/30/02
IG-55	24.6	42.029	36.4%	36.2%**	2/20/03
				36.8%	12/31/02
IG-541	26.1	46.480	34.1%	34.4%**	2/20/03
				34.1%	12/31/02
Nitrogen	28.5	51.364	31.9%	32.6%**	2/20/03
				32.2%	12/20/02
				31.0%	10/30/02
CO_2	37.5	83.672	22.4%	20.7%**	2/20/03
				20.9%	11/4/02

*T_e = 1871 K ** Witnessed by 3rd FM Global and UL Canada.

The results of determinations made on different dates are given to illustrate the repeatability of the procedure within one lab. An extinguishing test series for each agent was witnessed by two independent third parties* who verified that the procedure used was in accordance with the requirements of NFPA 2001 Appendix B and ISO 14520 Annex B.

An extinction temperature of 1871 K was calculated for the fuel-air-agent composition for the experimental nitrogen cup burner value (n-heptane fuel: Q = 4502.5 kJ/mol). This result is remarkably similar to the result obtained for nitrogen inerting of n-hexane-air pre-mixed flames. The values of agent enthalpy change from 298 K to T_e = 1871 K are given in Table 3 . A calculation of q_{Loss} for the case of nitrogen as agent was made, as done for the pre-mixed case, with the result that the value obtained was, again, less than 1% of Q. Again, q is small enough to neglect in further analysis. In the n-heptane-air case (n = 7) there are 56.36 moles of normal combustion products (exclusive of agent) and their enthalpy change from 298 K to T_e = 1871 K, ΔH_P, is 3240.1 kJ/mol fuel. Equation (9) can now be expressed, for the n-heptane case, as

$$X_G = \frac{\dfrac{1262}{\Delta h_G}}{52.36 + \dfrac{1262}{\Delta h_G}} = \frac{1}{0.0415\Delta h_G + 1} \qquad (11)$$

* The third party witnesses were FM Global (West Gloucester, RI) and Underwriters Laboratory of Canada (Toronto).

Equation (11) was used to calculate extinguishing concentrations for each of the several agents with the assumption that extinction temperature, T_e, is the same in each case. The results, given in Table 3 and compared to the measured values in Fig. 1 are in excellent agreement with

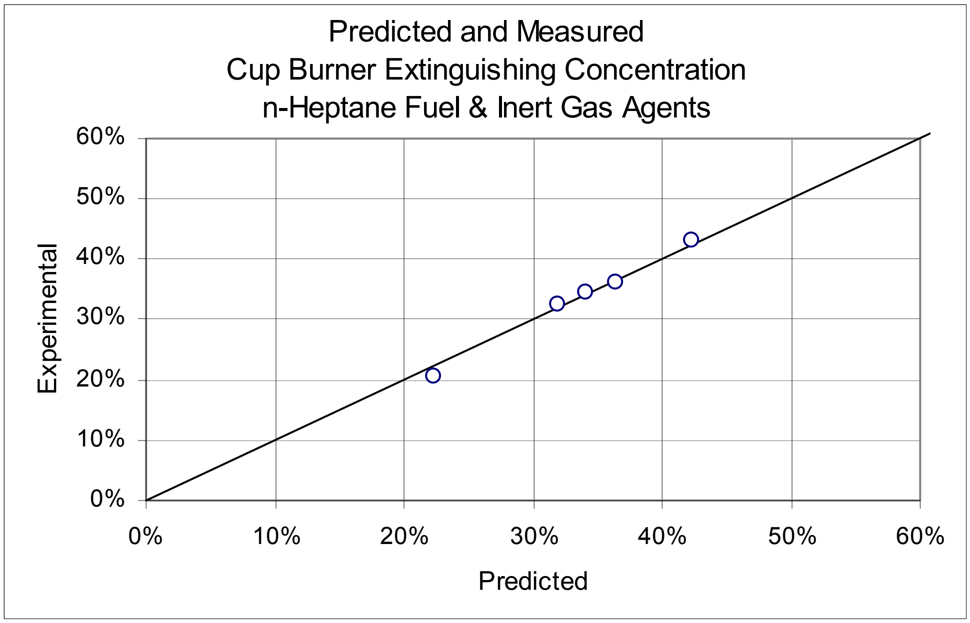

Figure 1. Comparison of predicted and measured cup burner extinguishing concentrations. Fuel: n-Heptane

measured values for inert gas agents from argon to carbon dioxide with heat capacities that vary from 20.8 to 37.5 J/mol-K. Thus, a coherent and self-consistent set of cup burner data are in complete agreement with the inert gas extinguishing theory.

CUP BURNER TEST METHOD IMPLICATIONS

The foregoing analysis indicates that the determination of the flame extinguishing concentration of an inert gas agent for a flammable liquid by the cup burner method is in agreement with theory and, as such, is a useful method in both extinguishing studies and regulatory guidance. Inconsistencies in public data, noted previously, point to the need for a careful review of the cup burner method with the goal of improving the definition of the apparatus and procedure so that lab-to-lab reproducibility can be achieved that is comparable to within-lab repeatability. Areas for potential improvement include specifications on cup design and fabrication materials, pre-burn, and step-wise agent addition, among others. The procedure should include a requirement for use of a benchmark agent, such as nitrogen or carbon dioxide. A proposal has been made to, and accepted by, the ASTM D-26 committee on *Halogenated Organic Solvents and Fire Extinguishing Agents* to conduct a review of the cup burner method and formulate it into an ASTM standard including sections on calibration, standardization, interferences, criteria for precision and bias that are presently lacking in the method.

CONCLUSIONS

The MEC values of inert gas extinguishing agents that appear in national and international standards exhibit inconsistencies that are relevant to safe design and market positioning of these products. A flame extinguishing model was developed that uniquely relates the MEC of an inert gas agent to its heat capacity. A new and coherent set of MEC data for three inert gases and two mixtures was obtained using an original ICI cup burner apparatus. The extinguishing results obtained using nitrogen served to identify the extinguishing limit temperature, T_e , a key parameter in the extinguishing model. The model was then used to make predictions of the MEC values of all inert gas agents. The predicted MEC values were in excellent agreement with experimental values. The data validates the theory, demonstrates repeatability, and supports the need to make enhancements in the cup burner method that will lead to improved inter-laboratory reproducibility. A recommendation has been made to the ASTM D-26 committee (which has responsibility for gaseous fire extinguishing agents) to review the cup burner method with the goal of developing an enhanced procedure having superior internal controls and inter-laboratory repeatability.

NOMENCLATURE

ASTM	American Society for Testing and materials
C or C_P	Heat capacity at constant pressure, J/mol-K
$\Delta h^o_{i,298}$	Standard enthalpy of formation of species *i* (298 K, 1 atm), kJ/mol
$\Delta h^o_{r,298}$	Heat of reaction per mole of fuel at standard conditions (298 K, 1 atm), kJ/mol
Δh_G	Enthalpy change, inert gas agent, 298 K to T_e, kJ/mol
ΔH_P	Enthalpy change, normal combustion products, 298 K to T_e, kJ/mol fuel
MEC	Minimum extinguishing concentration
n	Number of carbon atoms in an aliphatic hydrocarbon fuel species
q	Heat loss from flame, kJ/mol fuel
Q	Heat of combustion, kJ/mol fuel
T_e	Temperature at extinction, K
T_f	Adiabatic flame temperature, K
X_G	Mole fraction of added inert gas agent
$\nu_{Air,\ G}$	Stoichiometry coefficient of air or added inert gas, mol

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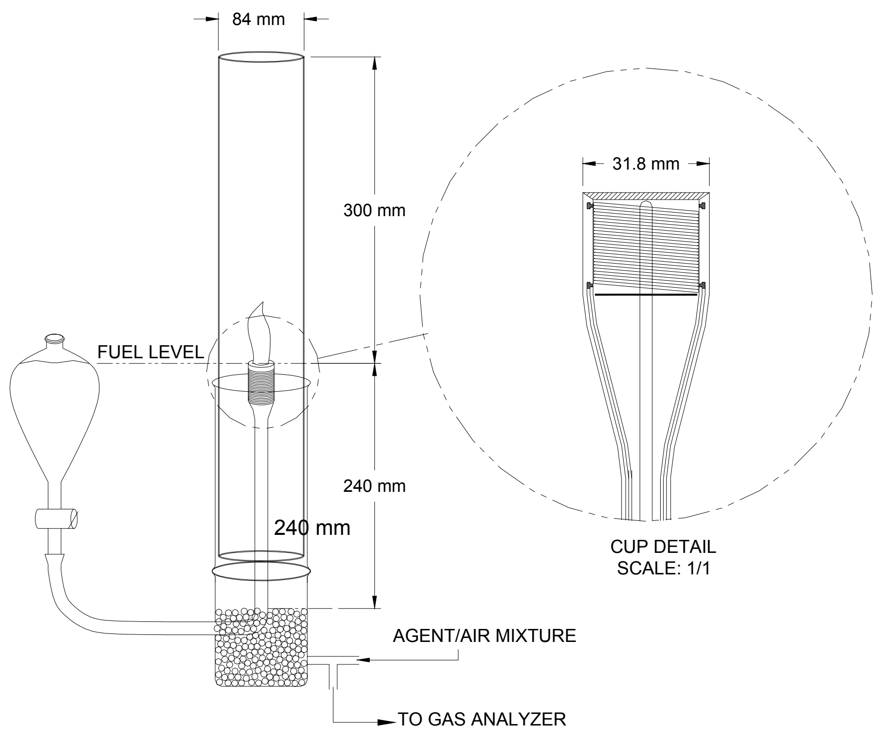
Annex A
Cup Burner: Apparatus & Procedure

General. The cup burner test procedure is used to make determinations of the concentration of a gaseous fire extinguishing agent in air which causes the extinction of the flame developed in a standard cup burner apparatus at stated conditions of fuel temperature and air flow rate. Tests are conducted at one or more specified flow rates. The apparatus and procedure described herein are in conformance with the requirements of ISO 14520 Annex B and NFPA 2001 Appendix B. The essential elements of the apparatus and method are summarized below.

Apparatus. The apparatus employed, shown schematically in the figure below, consists of several elements.



Cup. The fuel cup is made of a high-temperature glass or quartz. It has an outside diameter of 31.8 mm and a wall thickness of 4.8 mm ending in a 45 degree chamfer at the top leaving a lip edge width of 2 mm. The cup wall contains a platinum resistance wire which is employed in heating the fuel as required. The body of the cup has an overall length of 61 mm and tapers to a base diameter of 12 mm where it is fused to the fuel supply stem. The top of the cup is approximately 240 mm above the diffuser bed and 300 mm below the top of the chimney. The stem of the cup is connected to the fuel supply connection located in the diffuser bed.

Chimney. The chimney consists of a glass or quartz tube having an outside diameter of 90 mm, an inside diameter of 84 mm, and a height of ~520 mm. The chimney is seated on the diffuser assembly body which is fitted with ports for entry of air and fuel.

Fuel reservoir. Liquid fuel is placed in a funnel, with stopcock, or equivalent. The reservoir is supported adjacent to the cup burner assembly. The reservoir support has a means to precisely adjust and maintain the fuel liquid level. The fuel reservoir is connected to the fuel inlet port at the base of the diffuser assembly by means of flexible tubing.

Diffuser assembly. The diffuser assembly body supports the chimney about 10 mm above a bed of ~7 mm diameter glass beads and has entry ports for air and fuel. The depth of glass beads is approximately 75 mm and extends above the point of air and agent entry.

Air supply, flow control and measurement. Filtered air is supplied from a laboratory compressor. Pressure regulated air is passed to a flow regulating valve prior to entry into the air rotameter. Air then passes to a tee fitting where it is joined with the agent supply line.

Agent flow control. Inert gas agent is supplied from a high-pressure cylinder of certified composition. A pressure regulator and flow regulating valve is used to control the flow rate of agent gas. Agent then passes to a tee fitting where it is joined with the air stream. The agent-air mixture is passed to the cup burner through approximately 450 mm of 12 mm ID plastic tubing.

Rotameters. Two rotameters consisting of glass tubes with metal floats are used to measure gas flow rates. The rotameters were calibrated by a qualified independent laboratory.

Agent concentration. The concentration of agent gas in the agent-air mixture is determined by two independent methods: (a) from the flow rates of agent and air at the time of extinguishment as follows, and (b) by measurement of the oxygen concentration of the agent-air stream.

Oxygen Analyzer. A Nova Analytical Systems, Inc. Model 375WP flue gas analyzer is used to measure the oxygen concentration in the agent-air stream. The analyzer samples the combined agent-air mixture before it enters the cup burner apparatus. The sampling rate is approximately 0.9 liters per minute.

Procedure. The procedure used is as described in Appendix B of NFPA 2001 and Annex B of ISO 14520-1 and is not repeated here in full. These two procedures permit different ranges of pre-burn time. All tests conducted for this report used a pre-burn time of 90 s, common to both documents. At the end of the pre-burn period agent gas / vapor is added to the air stream. After agent addition to a fixed flow rate the flame is observed for approximately 10 s and not extinguished the agent flow rate is increased in steps, waiting 10 s after each adjustment, until extinguishment occurs.

All tests reported in this paper were carried out at an air flow rate of 40 liters/min, or a superficial air velocity of 0.120 m/s. A minimum of six tests were carried out at each air flow rate. The first test for each agent was used to establish the approximate agent flow rate to achieve extinguishment and the results therefrom were not considered in the final analyses.