

MAFF VALIDATED METHODS FOR THE ANALYSIS OF FOODSTUFFS

No.V6

ASH IN COCOA AND CHOCOLATE PRODUCTS

Correspondance on this method may be sent to R. Wood, Statutory Methods (Chemistry and Microbiology) Department, Ministry of Agriculture, Fisheries and Food, Food Science Laboratory, Food Safety Directorate, Norwich Research Park, Colney, Norwich NR4 7UQ

1. Scope and Field of Application

The method allows the determination of the ash content of cocoa mass; this is taken as a measure of total mineral content.

2. Definition

Ash content: the content of total ash as determined by the method specified.

3. Principle

The sample is ignited under controlled conditions to an inorganic carbon free residue: this residue is calculated as the total ash content.

4. Reagents

Wherever the use of water is required, distilled or water of equivalent purity is to be used.

4.1 Ethanol, 95% by volume.

4.2 Hydrochloric acid, dilute, approximately 7 g HCl/100 ml. Carefully add, with stirring to 500 ml water, 100 ml concentrated hydrochloric acid (HCl: $\rho_{20} = 1.18$ g/ml), and mix.

5. Apparatus

5.1 Incineration dishes, made of platinum or silica (ie materials not affected by the test conditions), and of 25-50 ml capacity.

5.2 Desiccator, containing freshly activated silica gel (with a water content indicator) or an equivalent desiccant.

5.3 Electric muffle furnace, air-ventilated, temperature controlled by thermostat at $600 \pm 25^{\circ}\text{C}$, fitted with a pyrometer.

5.4 Infra-red lamp

5.5 Water bath, boiling.

5.6 Analytical balance

6. Procedure

6.1 Preparation of the incineration dish

Clean the incineration dish, whether new or used, with boiling dilute hydrochloric acid. Rinse it free from acid with a large quantity of water. Heat it for 30 min. in the muffle furnace. Remove it from the furnace, allow it to cool to ambient temperature in the desiccator and weigh it to the nearest 0.1 mg (m_1). Not more than four incineration dishes shall be put in the desiccator at one time.

6.2 Test portion

Weigh into the prepared incineration dish to the nearest 0.1 mg, 2-5 g of the sample (m_0) such that the minimum expected total ash content is between 10 and 50 mg. Carbonise by either of the following procedures.

- (i) Place the dish and sample in the cold muffle furnace and slowly bring to temperature ($600 \pm 25^\circ\text{C}$) in a fume hood with the exhaust vent of the muffle furnace open or the door incompletely closed.
- (ii) Heat the dish and sample under an infra-red lamp until smoking ceases and then transfer to a heated muffle furnace.

Heat for 2 hr. at 600°C . Remove dish and place in desiccator to cool. When cool, remove from desiccator, moisten the ash with ethanol and dry under the infra-red lamp or on the water bath. Replace the dish in the muffle furnace and heat for a further hour. Remove dish and allow to cool to ambient temperature in the desiccator. When cool, weigh to the nearest 0.1 mg. Repeat the final step until the difference in two successive weighings is no greater than 1 mg. Let the final weighing be m_2 .

7. COSHH

Analysts are reminded that appropriate hazard and risk assessments required by the Control of Substances Hazardous to Health Regulations, 1988 (See "Control of Substances Hazardous to Health - Approved Code of Practice, Control of Substances Hazardous to Health Regulations, 1988") must be made before using this method.

8. Expression of Results

The total ash content, calculated as a percentage by mass of the sample, is given by:

$$\% \text{ total ash content} = \frac{m_2 - m_0}{m_1} \times 100$$

Where:

m_0 is the initial weight of sample to the nearest 0.1 mg;

m_1 is the weight of the incineration dish;

m_2 is the final weight of the incineration dish and carbonised sample.

The result is expressed as this percentage to two places of decimals.

9. References

- 9.1 HJ Judd, MD Percival and R Wood, J. Assoc. Publ. Analysts, 1984, **22**, 81-101
- 9.2 "Determination of ash in cocoa and chocolate products", International Office of Cocoa and Chocolate/International Sugar Confectionery Manufacturers' Association (IOCC/ISCMA), Analytical Methods 4a/1973 (previously OICC Analytical Method 4a/1973), London
- 9.3 Ministry of Agriculture, Fisheries and Food, Food Safety Directorate, MAFF Validated Methods for the Analysis of Food, Introduction, General Considerations and Analytical Quality Control, J. Assoc. Publ. Analysts, 1992, **28**, 11-16

APPENDIX 1

Analytical Quality Control

General principles of analytical quality control are outlined in protocol V0 of the series⁽³⁾.

A1 Repeatability

The absolute difference between two test results obtained under repeatability conditions should not be greater than the repeatability limit, r , deduced from the collaborative trial data summarised in Table 1. At about 3% ash, r may be taken to be 0.3% ash. This precision corresponds to a relative standard deviation of repeatability (coefficient of variance of repeatability), RSD_r , of about 3.8%.

A2 Reproducibility

The absolute difference between two test results carried out under reproducibility conditions should not be greater than the reproducibility, R , deduced from the collaborative trial data summarised in Table 1. R may be taken as 0.5% ash; this precision corresponds to a relative standard deviation of reproducibility (coefficient of variance of reproducibility), RSD_R , among different laboratories of about 6%.

A3 Trueness (Bias)

The collaborative trial established satisfactory precision parameters for the method, but its accuracy was not tested by spiking with known amounts of mineral. However, there is no reason to suspect any systematic bias.

A4 Limit of Detection

This limit has not been established, but the collaborative trial data suggests an accuracy which, if maintained, corresponds to a lower limit of roughly 0.3% ash for a single determination.

A5. Statistical Data Derived from the Results of Interlaboratory Tests

Participants in the collaborative trial each analysed six samples of cocoa mass once (three samples in blind duplicate). Each pair of samples had

been tempered and moulded into approximately 50 g size bars; only one pair (O/R) had been alkali-treated. The fat content was 56 - 57% by mass.

Table 1 summarises the statistical data; the ash levels were expressed as a percentage by mass of the sample.

TABLE 1
Statistical Analysis of the % Total Ash Cocoa Mass Samples

Sample	N/S	O/R	P/Q
Number of Laboratories retained after eliminating Outliers	17	16	17
Number of Laboratories eliminated as outliers	1	2	1
Number of results accepted after eliminating outliers	34	32	34
LEVEL OF ANALYTE			
Mean observed value $\bar{x}$	2.81	3.34	2.83
REPEATABILITY			
Standard Deviation s_r	0.09	0.08	0.11
Relative Standard Deviation RSD_r (%)	3.2	2.4	3.8
Repeatability r [$2.8 \times S_r$]	0.25	0.22	0.30
REPRODUCIBILITY			
Standard Deviation S_R	0.13	0.18	0.16
Relative Standard Deviation RSD_R (%)	4.7	5.2	5.8
Reproducibility R [$2.8 \times S_R$]	0.37	0.49	0.46

A6 Key to Table 1

Symbol	Definition
$\bar{x}$	Overall mean value
S_r	The standard deviation of repeatability
RSD_r	The relative standard deviation of repeatability, expressed as a percentage of the mean (coefficient of variance of repeatability CV_r)
r	Repeatability
S_R	The standard deviation of reproducibility
RSD_R	The relative standard deviation of reproducibility, expressed as a percentage of the mean (coefficient of variance of reproducibility CV_R)
R	Reproducibility