

## **Analysis of the Effluent Released from Wheat and Soybeans during Heating**

ROBERT IDEN and ROBERT LIVINGSTON, Battelle Memorial Institute, Columbus, Ohio 43201, and C. A. WATSON, Market Quality Research Division, ARS, USDA, Manhattan, Kansas 66502

### **ABSTRACT**

Analyses of effluents released from wheat and soybeans under conditions simulating moisture-content determinations were performed in vacuum, air, and helium. The compounds released with the moisture were identified and measured quantitatively. None of the compounds released with the moisture would interfere with various instrumental techniques that might be used to measure moisture in grain.

Prior to the selection of a basic principle to develop an instrument that would measure both content and distribution of moisture in a grain sample, it was

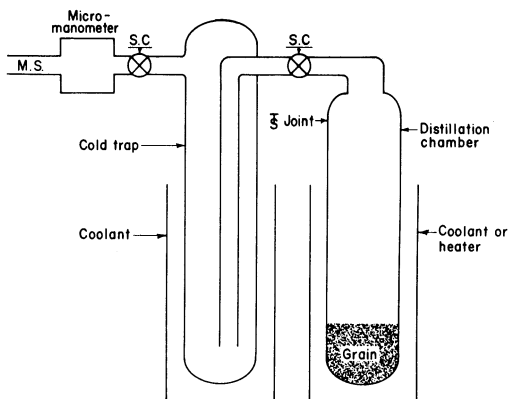


Fig. 1. Grain distillation apparatus.

advisable to know the qualitative and quantitative aspects of compounds released with the moisture. Thus, possible errors, involved in any principle that might be selected for the moisture meter, could be evaluated. Determination of moisture distribution in a grain sample, by necessity, must be on a kernel-by-kernel basis and, therefore, creates many perplexing problems.

Bidwell and Sterling (1) criticized oven methods for moisture determination for several reasons, among which was driving off volatile substances other than water. Little information is available on the amount and identity of these substances. Hart and Neustadt (2) suggested that phospholipids were volatilized from soybeans and flaxseed when heated at  $130^{\circ}\text{C}$ . Samples heated in a water oven contained amines, whereas they were absent in unheated samples. Hart and Golumbic (3) reported that an oily substance was given off from several seeds heated under vacuum at  $80^{\circ}\text{C}$ . Some seeds decompose when heated to  $130^{\circ}\text{C}$ ., giving off carbon dioxide and water (3).

#### MATERIALS AND METHODS

A detailed cryogenic and heated distillation at 12 temperatures from  $-80^{\circ}$  to  $+150^{\circ}\text{C}$ . was used to isolate individual or groups of compounds released from SRW wheat. These compounds were eluted into a calibrated volume equipped with a micromanometer to determine the total effluents at each step of the distillation. This collection system was an integral part of an inlet to a mass spectrometer used to identify and determine the amount of each component in the total effluent. Standard methods of calculating the data were employed; e.g., ref. 4. The apparatus used is shown in Fig. 1.

Twelve grams of SRW wheat containing approximately 13% moisture, dry basis, was cracked and placed in the distillation chamber; the air was evacuated quickly from the system. The wheat was cooled to  $-196^{\circ}\text{C}$ . and evacuation continued to approximately  $10^{-5}$  torr. The distillation chamber was warmed to  $-80^{\circ}\text{C}$ . and the distillate collected in a  $-196^{\circ}\text{C}$ . trap. The noncondensables in the trap and in the chamber were measured and analyzed. These noncondensables were pumped from

TABLE I. EFFLUENTS FROM WHEAT HEATED IN VACUUM  
(AIR COMPONENTS)

Grain Temp. °C.	CO <sub>2</sub> γ/g. wheat	Ar γ/g. wheat	O <sub>2</sub> γ/g. wheat	N <sub>2</sub> γ/g. wheat	H <sub>2</sub> γ/g. wheat	Total γ/g. wheat
-80	6.5	2.6	40.0	124.0	...	173.10
-15	0.55	<0.01	0.29	1.2	...	2.04
27	2.0	0.47	8.0	25.0	...	35.47
40	1.30	0.14	2.0	10.3	<0.01	13.74
50	0.43	<0.01	0.05	0.04	<0.01	0.52
75	2.50	<0.01	0.06	0.53	<0.01	3.09
100	6.70	0.01	0.04	0.13	0.01	6.89
110	5.20	0.02	0.03	1.20	0.01	6.46
120	18.0	0.12	1.60	6.40	0.01	26.13
125	211.0	1.2	0.64	5.10	0.01	217.95
130	22.0	...	...	0.14	<0.01	22.14
150	144.0	...	...	0.17	<0.01	144.17
Totals	420.18	4.56	52.71	174.21	0.04	651.70

the system and the distillation chamber was isolated from the cold trap. The trap temperature was increased to -80°, -15°C., and to ambient temperature with the noncondensables measured, analyzed, and pumped off at each temperature. The four cold-trap temperatures were used to provide additional separation of individual compounds or groups of compounds. The grain temperature was increased to -15°C. and the effluent was again collected in a -196°C. trap. The same procedure was used to identify and measure the noncondensables for the four temperatures of the cold-trap and was repeated for each grain temperature shown in Tables I and II. No attempt was made to measure the amount of water released. The collected water was discarded occasionally after mass spectrometric analysis. A separate

TABLE II. EFFLUENT FROM WHEAT HEATED IN VACUUM  
(COMPONENTS OTHER THAN AIR COMPONENTS)

Grain Temp. °C.	CH <sub>2</sub> O γ/g. wheat	C <sub>2</sub> H <sub>5</sub> OH γ/g. wheat	CH <sub>3</sub> Cl γ/g. wheat	CO γ/g. wheat	H <sub>2</sub> S γ/g. wheat	NH <sub>3</sub> γ/g. wheat	CH <sub>3</sub> CHO γ/g. wheat	Total γ/g. wheat
27	0.08	...	...	...	...	...	...	0.08
40	0.01	...	...	...	...	...	...	0.01
50	0.01	...	...	...	...	...	...	0.01
75	<0.01	0.03	...	...	...	...	...	0.03
100	<0.01	0.11	...	...	...	...	...	0.11
110	0.54	0.03	...	...	...	...	...	0.57
120	0.05	0.87	...	...	...	...	...	0.92
125	0.90	0.48	0.23	...	...	...	0.04	1.65
130	0.06	1.20	0.03	0.98	0.44	0.01	...	2.72
150	0.02	8.90	0.15	0.57	0.47	3.70	...	13.81
Totals	1.67	11.62	0.41	1.55	0.91	3.71	0.04	19.91
Total Tables I and II								671.61

TABLE III. EFFLUENT FROM WHEAT AND SOYBEANS HEATED IN AIR, VACUUM, AND HELIUM

Grain Medium Temp.	Wheat, Air, 135	Wheat, Helium, 135	Soybeans, Vacuum, 150
$^{\circ}\text{C.}$	$\gamma/\text{g.}^{\text{a}}$	$\gamma/\text{g.}^{\text{a}}$	$\gamma/\text{g.}^{\text{a}}$
$\text{CO}_2$	296.0	66.0	1067.0
Ar	0.40	0.10	1.40
$\text{O}_2$	4.00	7.00	2.60
$\text{N}_2$	23.0	56.00	19.0
$\text{H}_2$	13.0	0.20	<0.01
$\text{CH}_2\text{O}$	0.02	0.05	.....
$\text{C}_2\text{H}_5\text{OH}$	1.00	0.80	0.22
m/e 41 and 43 <sup>b</sup>	2.00	.....	.....
$\text{CH}_4$	1.00	.....	.....
$\text{H}_2\text{S}$	0.20	0.03	1.85
$\text{CH}_3\text{CHO}$	5.00	.....	.....
Totals	345.62	130.18	1092.07

<sup>a</sup>Gram of wheat and soybeans.

<sup>b</sup>Unknown hydrocarbons.

analysis of this water showed only minor amounts of dissolved compounds, since the system operated at a comparatively low pressure.

After the compounds distilled from wheat under vacuum were identified, wheat was heated for 1 hr. at  $135^{\circ}\text{C.}$  in helium and in air without the complete detailed distillation. Two 5-g. samples of the same cracked SRW wheat were placed in separate containers. One was sealed with helium and the other with the air remaining inside. The apparatus used was the same as shown in Fig. 1. Both were submerged in a  $135^{\circ}\text{C.}$  oil bath for 1 hr. Each container was connected to a  $-15^{\circ}\text{C.}$  cold-trap to condense the moisture during heating and to maintain a more nearly constant pressure in the wheat chambers. After the heating, the  $-15^{\circ}\text{C.}$  trap was cooled to  $-196^{\circ}\text{C.}$  to remove the effluent from the chamber. The cold-trap contents were analyzed as explained above; the four temperature steps were used (Table III).

Soybeans, which might be expected to release more organic materials owing to their high oil and protein content, were examined for 1 hr. at  $150^{\circ}\text{C.}$  in vacuum (Table III).

## RESULTS AND DISCUSSION

Tables I and II show the types and quantities of effluent released from wheat at various distillation temperatures. Each quantity is the sum of effluent from the four cold-trap temperature-fractionation steps. Only components which were identified with a high degree of confidence are listed. Other components released, but only tentatively identified, were: 0.11 and 0.03  $\gamma$  of acetylene per g. at  $125^{\circ}$  and  $150^{\circ}\text{C.}$ , respectively. A small amount of unidentified material was released having major molecular fragments at mass-to-charge ratios of 41 and 43, and which totaled less than 0.1  $\gamma$  per g.

Detailed distillation from  $-80^{\circ}$  through  $+50^{\circ}\text{C.}$  included the four major

components of air plus small quantities of formaldehyde and hydrogen (Tables I and II). At 75°C., ethanol was the major organic component, along with carbon dioxide which showed a gradual increase through 120°C. The large quantity of carbon dioxide released at 125°C. was also the starting point for the liberation of methyl chloride, carbon monoxide, hydrogen sulfide, ammonia, and acetaldehyde. A second large release of carbon dioxide occurred at 150°C. Organic compounds released through 150°C. totaled only 0.001% by weight of the wheat on a dry basis. Carbon dioxide was the major component, exclusive of moisture, and was present at 0.04 weight % of the wheat. The major portion of the effluent was released between 120° and 130°C. (Fig. 2).

Table III shows the types and quantities of effluents released from wheat heated at 135°C. in air and in helium and from soybeans heated at 150°C. in vacuum. The effluent from the SRW wheat, heated in air and in helium at 135°C., showed a very small amount of organic materials and high carbon dioxide content (Table III). The carbon dioxide content of the total effluents released under air, vacuum, and helium was 85, 64, and 51%, respectively.

Contrary to expectations, because of their high oil and protein content, soybeans showed fewer organic components than the effluent released from wheat

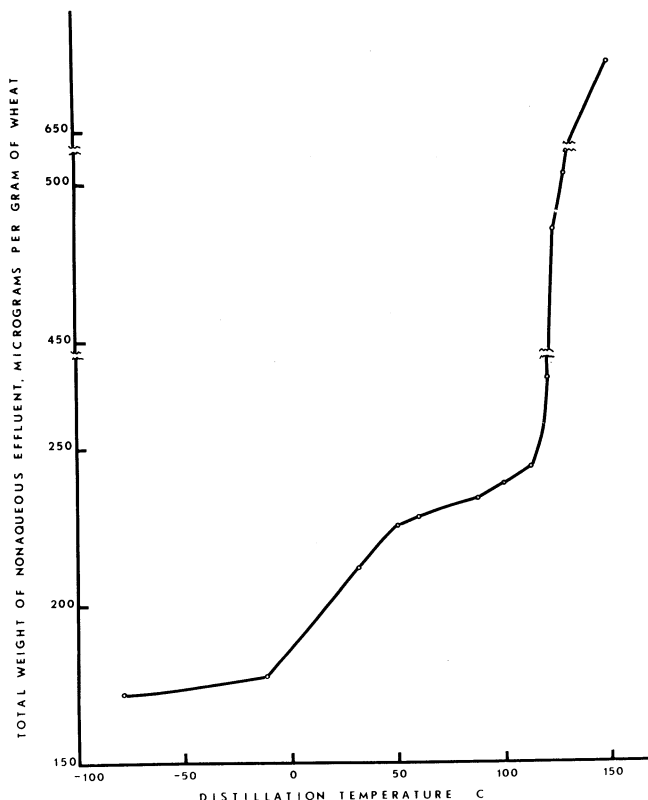


Fig. 2. Total effluent from wheat exclusive of moisture.

heated in vacuum at 150°C. The carbon dioxide content of the soybean effluent was 97.7% of the total effluent.

The original moisture content of the soybeans determined by the air-oven method (1 hr. at 135°C.) was 12.2% dry basis. The moisture content, based on the weight loss during the effluent evolution, was 14.7% dry basis, but the temperature was higher (150°C.) than that used in the air-oven method.

### CONCLUSIONS

Heating SRW wheat in air, helium, and vacuum showed no significant amount of organic material or inorganic material which would produce a meaningful error in various instrumental techniques that might be used to measure moisture in wheat.

The total effluent released from soybeans, exclusive of water, showed fewer organic components than the effluent from wheat, and the total material released would not affect moisture determination significantly.

Many instrumental and chemical techniques are available for the analysis of moisture in grain. The identification and quantification of effluent components other than moisture should permit a better evaluation of possible errors involved in these or future instrumental techniques, if some trace compounds greatly affect a particular method.

These data could also serve as a foundation for additional studies which might lead to a basic understanding of the internal chemical changes in grain during dehydration.

### Acknowledgment

This work was performed as part of a research program sponsored by the Market Quality Research Division, Agricultural Research Service, United States Department of Agriculture.

### Literature Cited

1. BIDWELL, G. L., and STERLING, W. F. Preliminary notes on the direct determination of moisture. *J. Assoc. Offic. Agr. Chemists* 8: 295 (1924).
2. HART, J. R., and NEUSTADT, M. H. Application of the Karl Fischer method to grain moisture determination. *Cereal Chem.* 34: 26 (1957).
3. HART, J. R., and GOLUMBIC, C. A comparison of basic methods for moisture determination in seeds. *Proc. Intern. Seed Testing Assoc.* 27: 907 (1962).
4. BARNARD, G. P. *Modern mass spectrometry*. The Institute of Physics: London (1953).

[Received March 28, 1969. Accepted July 18, 1969]