SILO GAS: PRODUCTION AND DETECTION[1]

W.S. Reid[1], J.E. Turnbull[1], H.M. Sabourin[2], and M. Ihnat[3]

[1]Engineering and Statistical Research Institute, Research Branch, Agriculture Canada, Ottawa, Ontario K1A 0C6; [2]Roche Associés Ltée., Sainte-Foy, Québec G1V 4M3; and [3]Chemistry and Biology Research Institute, Research Branch, Agriculture Canada, Ottawa, Ont. K1A 0C6.

Contribution no. I-552 received 24 November 1983, accepted 26 September 1984.

Reid, W.S., J.E. Turnbull, H.M. Sabourin, and M.Ihnat. 1984. Silo gas: Production and detection. Can. Agric. Eng. 26: 197–207.

Previous research on silo gas production, properties, danger to humans and detection methods are reviewed. A survey of Quebec silos just after harvest showed that eight out of 39 silos contained one or more of the gases CO_2, NO or NO_2 at concentrations above the short-term exposure limits for safety of workers. Gas detection experiments included the use of continuous recorders for CO_2 and NO_2, and chemical tube detectors for CO_2, NO_2 and NO + NO_2 (NO_x). Continuous recorders were useful for research but are too costly for general farm use. Four NIOSH-approved chemical tube detectors were tested; of these, the "Dräger" tubes and hand-operated bellows pump were the most convenient and rapid to use. Tube detectors close-coupled to the corresponding hand pump were sufficiently accurate, but for remote testing in deep silo headspaces, extension tubes up to 20 m long are sometimes necessary. With these long connecting tubes, extra pump strokes and excessive testing time are necessary. The tube detector method needs more laboratory calibration and field testing before it can be generally recommended for checking farm silos.

BACKGROUND

Silo gas is well known as a safety hazard for silo operators. The total number of accidental deaths due to silo gas is small, but silo gas accidents have frequently involved the original victim and would-be rescuers as well. Impaired lung efficiency and health (although not well documented) are also believed to be common problems for silo operators.

This paper reviews previous research and reports recent results on silo gas production and detection. This recent research is related primarily to short-term safety, rather than long-term health maintenance. This paper covers a field survey of silo gas production (using both tube detectors and continuous recorders in 39 silos) as well as laboratory tests of gas detectors (using four commercial detectors, with two different lengths of extension tube for remote detection, in two operational modes).

Silo Gas Characteristics

The principal hazardous gases produced in silos during the silage-making process are carbon dioxide (CO_2) and the various oxides of nitrogen, including nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2). These silo gases formed within the porous silage mass are denser than air. When new silage settles down into the silo, the gases are squeezed out of the silage mass into the silo headspace, displacing the air above the silage surface. In conventional open-top silos with loosely-fitted dome roofs, these dangerous gases tend to accumulate in greater concentrations at the lower regions of the headspace (Commins 1971). Unless the silo has a tight roof, wind blowing through roof and chute openings can ventilate the headspace above the settled silage, thus diluting the hazardous gases (at least in the top of the headspace). If the gases accumulate up to the level of a wall opening (such as an open chute door) they can overflow and spill down the chute into the connecting feedroom. In sealed-top silos the entire headspace can become more or less uniformly filled with silo gases (Schrottmaier 1982).

Carbon dioxide (CO_2) is an end-product from all life respiration processes. It comes from the dying plant tissue of the chopped crop and the various acid-forming bacteria associated with the ensiling process. When a crop is placed and packed into a reasonably airtight silo, the atmospheric oxygen contained in the silage mass is quickly consumed, yielding CO_2 and water, and the less-dense atmospheric nitrogen is displaced upwards.

The principal danger with CO_2 in silos and similar enclosed spaces is that it replaces the oxygen of the air (normally about 20% oxygen, 79% nitrogen, 0.03% carbon dioxide). Carbon dioxide is a dense gas (1.53 times air density) without color, odor or taste. Humans and farm animals fortunately have a built-in warning system for CO_2; when it reaches a certain concentration in the bloodstream, it triggers a nervous impulse and the victim 'gasps for air'. However, at the very high concentrations frequently encountered in unventilated silos, this reflex action can be inhibited and the victim is then asphyxiated (Anonymous 1977).

Oxides of nitrogen (N_2O, NO and NO_2) can be produced in dangerous quantities as a result of any weather condition, cultural practice or silage additive that leads to unusually high dissolved nitrate (NO_3) concentrations in the plant material. For example, a period of drought just before harvest (sometimes followed by abundant rainfall) can cause increased concentrations of dissolved NO_3 in the harvested crop (Scaletti 1965). Other factors that can increase the nitrate content of silage are immature crop, nitrogen fertilizer or manure overdose, black soils high in organic matter (Scaletti 1965), and nitrogenous silage additives such as sodium nitrate (Petersen et al. 1958).

Nitrous oxide (N_2O), sometimes called 'laughing gas', has been used as a medical anesthetic. As shown in Fig. 1 (from Wang and Burris (1960)), it can represent up to 4 or 5% of the gases contained within new silage material. It is not considered a significant risk to silo operators.

Nitric oxide (NO), on the other hand, is considered dangerous for two reasons. As NO it is dangerous in its own right (see Table I). In addition, it is easily oxidized in the presence of oxygen to the more dangerous nitrogen dioxide (NO_2) wherever suitable conditions are found such as in the partly-ventilated silo headspace or in the feedroom and connecting stable.

Nitrogen dioxide (NO_2) is a dense gas (1.58 times air density), seen as red to yellowish-brown fumes, with an odor described as acrid or bleach-like. When inhaled, it goes into solution with moisture on the wetted internal surfaces of the

[1]Research was funded through Agriculture Canada's AERD Contracting-out Program, Contract File 35SZ.01843-0-ME09, and was carried out by Roche Associés Ltée., Sainte-Foy, Québec, G1V 4M3.

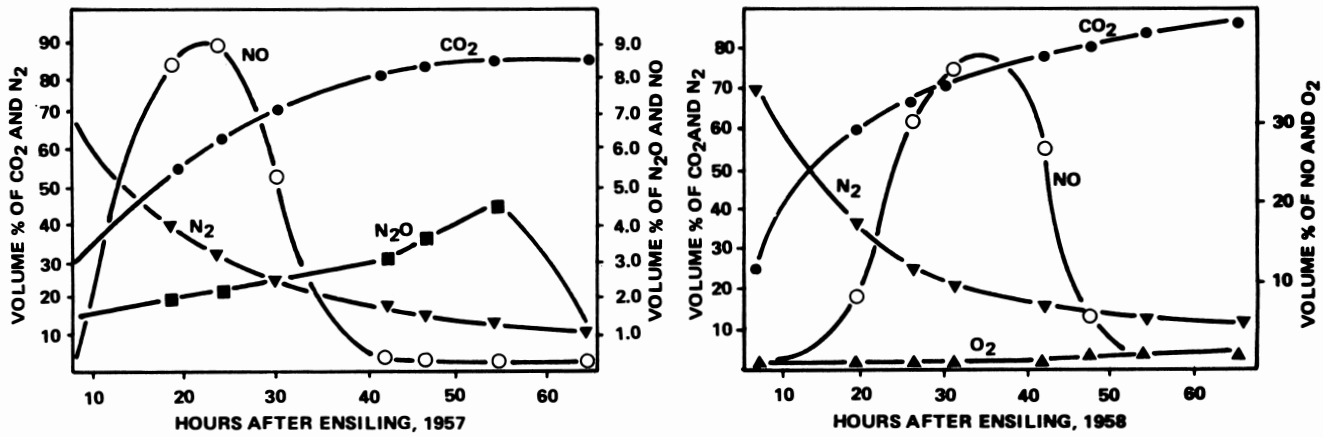

Figure 1. Gases within corn silage from a 3.7 × 12-m University Silo (from Wang and Burris (1960) reproduced by permission of L.C. Wang and J. Agric. Food Chem.)

TABLE I. THRESHOLD LIMIT VALUES (TLV) FOR SILO GASES (ANONYMOUS 1980)

Gas	TLV-TWA† (ppm)	TLV-STEL‡ (ppm)
Carbon dioxide (CO_2)	5000	15 000
Nitric oxide (NO)	25	35
Nitrogen dioxide (NO_2)	3	5
Oxides of nitrogen (NO_x)§	3	5

†Threshold limit value – time weighted average.
‡Threshold limit value – short term exposure limit.
§These values represent the authors' worst-case assumption that all of the NO_x converts to the more-toxic NO_2.

lungs, quickly forming potent nitric acid ($4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$; Partington 1957). This acid can burn the sensitive oxygen-transfer surfaces of the lungs, effectively stopping any further oxygen supply to the body. The usual result is permanent lung damage or death.

Other gases may be found, such as ammonia (NH_3) from adding anhydrous ammonia, and hydrogen cyanide (HCN) from some silages such as sorghum. However, both of these gases are lighter than air and are probably dispersed by natural ventilation.

Silo Gas Production Literature Review

Hayhurst and Scott (1914) reported a silo death, then attributed to carbon dioxide. Dubrunfaut (1868) first identified oxides of nitrogen as products of fermentation in natural biological material. These were later recognized as being toxic by Nichols (1930) and Van Oettigen (1941). Peterson et al. (1949) reported that a gas sample from the floor level of a silo-connected feedroom contained 151 ppm nitrogen oxides (expressed as NO_2). At that time the allowable NO_2 concentration in industrial environments was 25 ppm. Later, Peterson (1958) reported NO_2 gas concentrations up to 100 000 ppm (10%) flowing from a juice sampling pipe placed within the silage. Delaney et al. (1956), Lowry and Schuman (1956), and Grayson (1956) related 'silo filler's disease' or 'nitrogen dioxide pneumonia' to exposure to NO_2 gas in silos. Epidemiological investigations by Vigdortschik et al. (1937), Kennedy (1972), and Kosmider et al. (1972) have suggested the possibility of chronic pulmonary effects in humans exposed to oxides of nitrogen.

Scaletti et al. (1960, 1965) found that of 554 farm sites surveyed in Minnesota, 42% contained NO_2 in the feedroom (and by inference, the silo headspace). They also found that NO_2 production was clearly linked with silage produced from soils high in organic matter. Peterson et al. (1958) compared nitrate-type versus amino-acid-type additives in silage, finding that the nitrate additives produced 10 times as much nitrogen oxide gases as amino acid additives of equivalent N content.

Wang and Burris (1960) measured silo gas concentrations within newly-made corn silage (Fig. 1). Carbon dioxide content increased progressively with time after silo filling, and levelled off at over 80% within 50–60 h, apparently displacing upwards most of the less-dense atmospheric nitrogen. Of particular interest is the nitric oxide (NO) which, in their 1957 study, peaked at 9% after 23 h, and in 1958 at 4% after 30 h. As stated previously, NO is highly unstable; in contact with air it rapidly oxidizes to NO_2. This reaction would not proceed in the sealed atmosphere of an oxygen-limiting silo, but in the partly-ventilated headspace of a conventional silo, NO_2 can be produced in abundance.

Commins et al. (1971) showed that CO_2 gas concentrations in conventional tower silos decreased with increasing height above the silage surface, as would be expected for gases heavier than air (Fig. 2). They also covered the silage with a plastic sheet 5 days after filling the silo, and 1 day later checked gas levels. In spite of the cover, concentrations of NO, NO_2 and CO_2 had increased markedly around the periphery of the silo at 0.3 and 1.5 m above the silage surface. Apparently gases produced in the silage mass below the cover were squeezed out around the edge of the cover and could still endanger any-

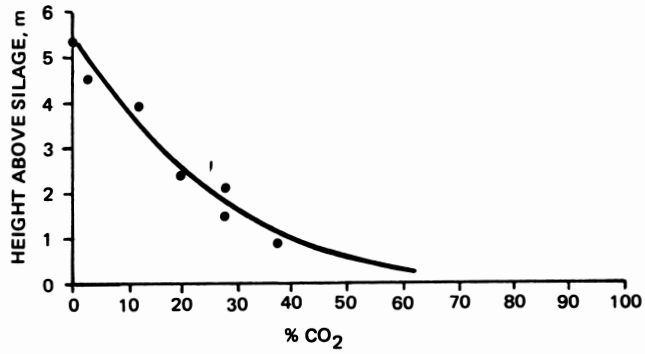

Figure 2. Variation in CO_2 concentration with height above silage (from Commins et al. (1971), reproduced by permission of B.T. Commins).

one entering the silo. In a 'sealed' silo (unlike the conventional silo with some natural ventilation at the top of the headspace), Schrottmaier (1982) observed no stratification of CO_2 or NO and NO_2 combined (termed NO_x) for headspace depths to 3.5 m.

In the U.S., safe limits of human exposure to various harmful substances have been established (Anonymous 1980); see Table I. The TLV-TWA (Threshold Limit Value–Time Weighted Average) values are the upper safety limits for workers repeatedly exposed for the typical 8-h workday (as, for example, a worker doing a lengthy repair on the silo unloader). Somewhat higher limits, TLV-STEL (Threshold Limit Value–Short Term Exposure Limit) are allowed for up to four daily exposures of 15 min separated by 1-h periods of no exposure (as, for example, a worker climbing the silo to remove a chute door) and the TLV-TWA must not be exceeded.

It would be desirable to be able to predict for tower silos the rates and depths of silage consolidation, and the corresponding rates and quantities of hazardous gas production. Such predictions could possibly lead to more precise calculation of silo headspace ventilation requirements for safety. Whittenbury et al. (1967) outlined the chemistry of many of the fermentation processes in silos, including the desirable formation of lactic acid (and some acetic acid) from the soluble carbohydrates in the fresh silage material. They explained the frequent problems encountered when making legume silage compared with grasses, due to the low sugar content as well as the high buffering capacity of the organic acids (especially glyceric acid) in clovers. Thus, in clovers about twice the quantity of lactic acid must be produced to bring the pH down to 4.0. They also outlined why excessively wet grass-legume silage (over 70% moisture) is attacked by clostridia under anaerobic conditions, destroying the valuable plant proteins. Another complicating factor is the inability of silos with cracks and leaks to achieve anaerobic conditions quickly after being filled, also resulting in protein degradation.

It is apparent from the variety and unpredictability of these fermentation processes that production rates and total accumulations of CO_2 and NO_x can not be accurately predicted at this time. Therefore one should always assume the presence of gas in dangerous concentrations and develop safety recommendations accordingly.

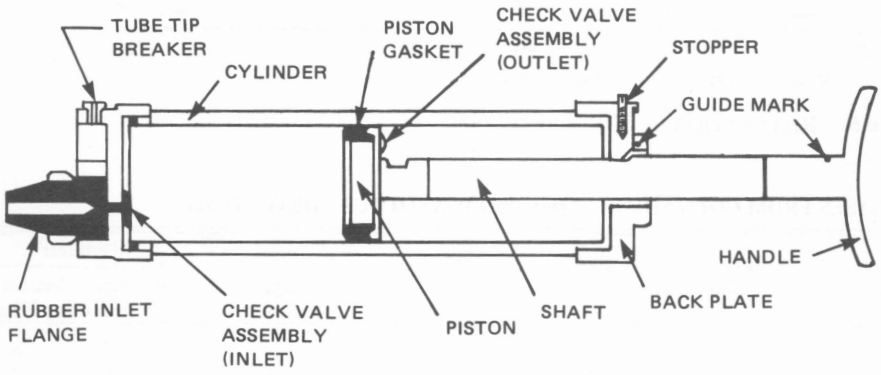

Figure 3. Piston and cylinder type gas detection pump (Gastec).

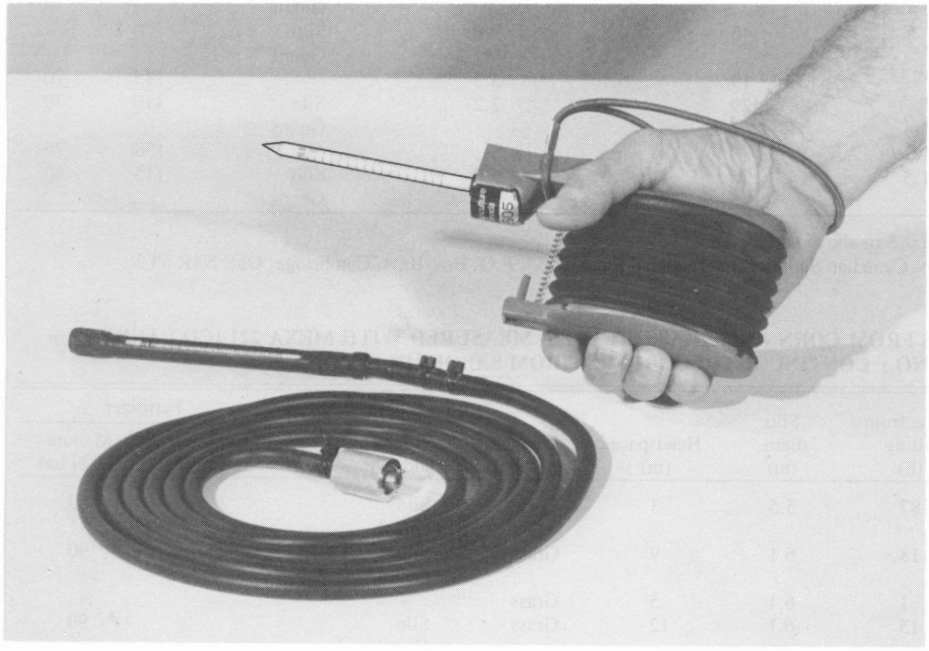

Figure 4. Dräger gas tester consisting of bellows pump, attached chemical tube and 5.5-m extension hose for remote sampling.

GAS PRODUCTION FIELD SURVEY

Procedures

A field survey of gas production in tower silos was conducted in Quebec, from 15 Aug. 1980 to 30 Oct. 1980 (corn harvest), and from 15 June 1981 to 30 Oct. 1981 (grass and corn harvests). In total, 39 silos equipped with various silage distributors and filled with grass-legume mixtures or corn, were tested for CO_2 and/or NO_2. A demand-type life support breathing apparatus was worn inside the silos, although Wells (1980) recommends the safer pressure-demand type with full-face mask.

Gas measurements were taken with chemical tube detectors attached to the corresponding hand pumps from the same manufacturer. Piston-type and bellows-type pumps were used. Figure 3 shows one of the three piston-type pumps (Gastec), and Fig. 4 shows the one bellows-type (Dräger). The tubes and their corresponding hand pumps have been approved by NIOSH (National Institute of Occupational Safety and Health, 944 Chestnut Ridge Road, Morgantown, W.V. 26505). Some silos (judged more likely to produce oxides of nitrogen) were also checked for NO_2 using the appropriate colorimetric tubes. Sampling height was 0.3 m above the silage surface, a point corresponding to a workman repairing the silo unloader. Other factors recorded were silo diameter, headspace depth, silage surface topography, time from last filling and prior nitrogen fertilization of the growing crop.

Of the 39 silos, five silos owned by cooperating farmers were also instrumented with continuous recorders for CO_2 (Mexa, model 221, Horiba Instruments Inc., 1021 Duryea Avenue, Irvine, Calif. 92714) and/or NO_2 (Ecolyzer model 7230, Ecolyzer Energetics Science Co., 85 Executive

Blvd., Elmsford, N.Y. 10523). Gas levels were continuously monitored for periods up to 48 h.

Results and Discussion — Field Survey

Of 39 silos surveyed, 24 showed detectable levels of the silo gases, and of these, nine were found to have gas levels in the danger zone (at or above TLV-STEL levels). Seven of the silos were investigated after the assumed 3-wk period of fermentation, and this may explain why some silos were found to be 'safe'. Where silos showed gas concentrations at or above the TLV-TWA, these results are given in Table II (tube detectors) and Table III (continuous recorders).

Gas production was observed to start as soon as 1 h after filling (silo 25, Table III) and gas remained to at least 100 h after filling (silo 5, Table II). This in general agrees with results from Wang and Burris (1960), (Fig. 1). The highest individual gas concentrations recorded with chemical tube detectors were 12% CO_2 (silo 12), 5 ppm NO_2 (silo 21) and 20 ppm NO (silo 21). Silo 35 indicated 17 ppm NO_x. All of these readings are potentially dangerous. In comparison, Commins et al. (1971) found gas levels as high as 60% CO_2 and 1920 ppm NO_2. Maximum concentrations could not be determined from the continuous recorders (as shown in Table III and Fig. 5) because, for three of the five silos instrumented, the gas concentrations went off scale at 15% CO_2 and 10 ppm NO_2 (well above the TLV-STEL level for the particular gas). Future research would be improved by sampling at several specified heights and locations over a recorded period of time.

The data for nitrogen fertilization (Tables II and III) are insufficient to correlate with silo NO_x concentrations. However, in some cases fertilization was very high, and these same silos produced nitrogen oxides.

Peterson et al. (1958) found that silage additives such as sodium bisulphite ($NaHSO_3$) can reduce production of CO_2 and NO_2. Tables II and III show that of

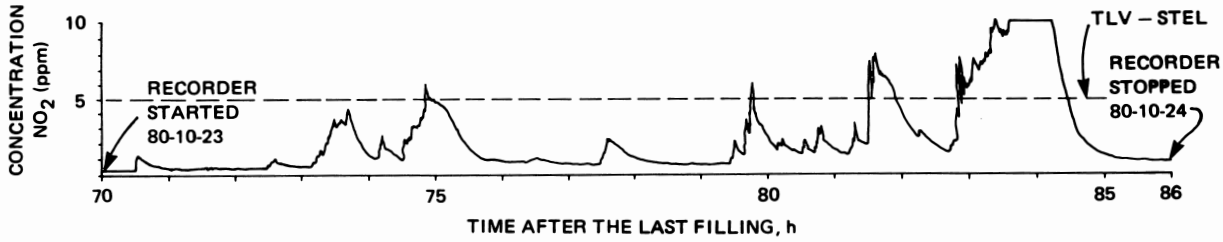

Figure 5. Recorder chart for NO_2, silo 21, 1980.

TABLE II. FIELD SURVEY OF GASES FROM CORN SILAGE, MEASURED WITH TUBE DETECTORS

Silo no.	Gas concentration CO_2 (%)	NO (ppm)	NO_2 (ppm)	NO_x (ppm)	Time from filling (h)	Silo diam. (m)	Head-space (m)	Silage additive	Fertilizer Inorganic (kg N/ha)	Fertilizer Manure (kg N/ha)
5			5		96	4.8	3.0	–	132	58
7	7.0 5.0†				18	5.5	7.0	–	110	50
12	12.0				70	4.8	7.0	–	16	30
16	0.15				47	4.8	14.0	Silo‡ Guard	78	60
17	0.15				46	4.8	9.0	Silo Guard	–	–
18	0.4	8	4		19	6.1	3.3	–	115	70
21	0.4	20	5		29	6.1	2.2	Silo Guard	110	70
35	8.0		3	17	8	5.5		–	138	70
38	0.5			1.5	26	7.3	5.0	Silo Guard	115	40

†Measured 1.0 m above silage surface. All others read at 0.3 m above surface.
‡Silage preservative, principal ingredient sodium sulphate. Canadian Supplier: International Stock Food, P.O. Box 1024, Cambridge, Ont. N1R 5Y2. (519) 622-2730.

TABLE III. FIELD SURVEY OF GASES FROM CORN AND GRASS SILAGES, MEASURED WITH MEXA 221 (CO_2) AND ECOLYZER 7230 (NO_2) CONTINUOUS RECORDERS (FROM SABOURIN 1983)

Silo no.	Gas concentration CO_2 (%)	NO_2 (ppm)	Time from filling (h)	Silo diam. (m)	Headspace (m)	Silage material	Silage additive	Fertilizer Inorganic (kg N/ha)	Fertilizer Manure (kg N/ha)
21		10+	87	5.5	3	Corn	Silo Guard	15	40
23	15+	10+	18	6.1	9	Grass	Silo Guard		90
25	6		1	6.1	5	Grass	–		
26	15+	10+	15	6.1	12	Grass	Silo Guard		90
32	1.5		4	5.5	2	Corn	–	60	106

+ Indicates actual value greater than the limits of the recording device.

eight silos chosen by the farm owners for treatment with Silo Guard (sodium sulphate), five produced NO_2, with three at concentrations greater than 5 ppm (the TLV-STEL level). Too few data are available here to show if there is any effect on gas production; however, at the 1:1000 dosage recommended for 'Silo Guard', it did not have any obvious effect.

Figures 5, 6, 7, 8 and 9 show some typical records, for silos 21, 23, and 26. Recordings from silo 21 (Fig. 5) show considerable variation in NO_2 concentration (from 0.5 ppm to over 10 ppm), believed to be primarily due to wind periodically removing the NO_2. Further research is needed to confirm this.

Silo 23, with a 9-m-deep headspace, at 19 h after filling was ventilated for 20 min with the forage blower. The NO_2 concentration could not be reduced under 10 ppm (maximum scale for the recorder), and CO_2 concentration (Fig. 7) rose to over 15% within 0.5 h after ventilation was stopped at about 19 h. Later (after 25 h) some rapid changes in CO_2 concentration occurred, probably due to windy conditions causing natural ventilation in the silo headspace. For the period between 30 and 36 h (Figs. 6 and 7), both gas concentrations were again reduced (windy conditions) but subsequently stayed low for 22 h, at which time the recorders were removed. The NO_2 and CO_2 recorders were recalibrated at 36 and 35.8 h, respectively, which may account for an apparent abrupt increase in recorded CO_2, possibly due to instrument drift. Natural ventilation and declining gas production rates could easily explain the low gas levels found after 3 wk in seven of the silos tested.

Silo 26 was ventilated at about 20 h after filling and prior to installation of the CO_2 and NO_2 recorders; the curves in Figs. 8 and 9 demonstrate how rapidly both gases can accumulate after ventilation is stopped. Detectable levels of CO_2 showed up 0.5 h after ventilation, rising far above TLV-STEL level of 15 000 ppm (1.5%) in just over 1 h. Nitrogen dioxide (NO_2) accumulated somewhat more slowly,

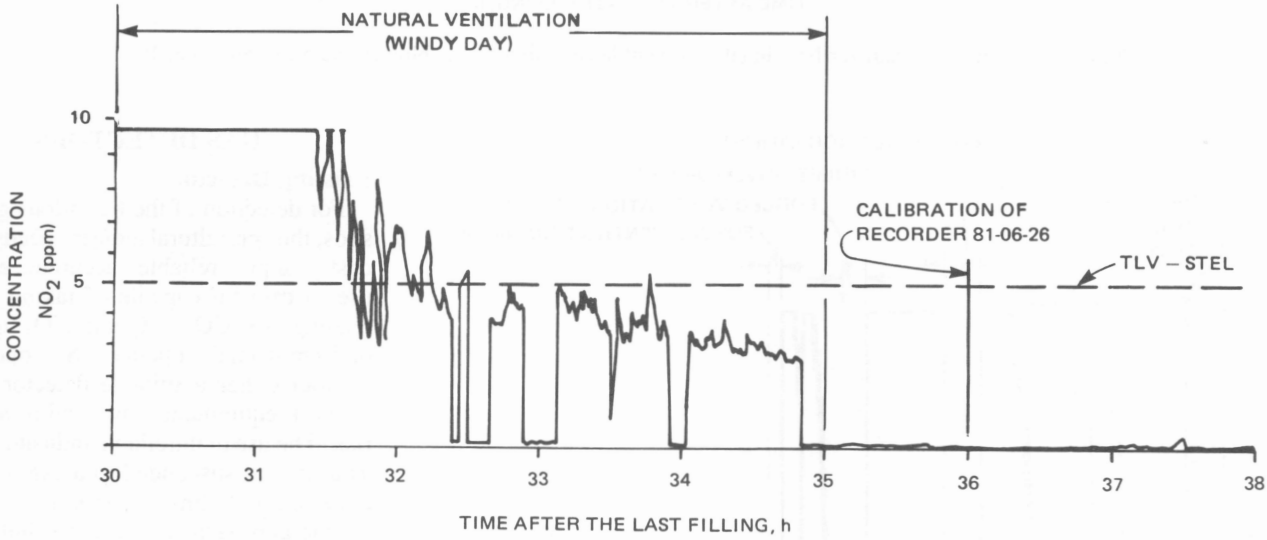

Figure 6. Recorder chart for NO_2, silo 23, 1981.

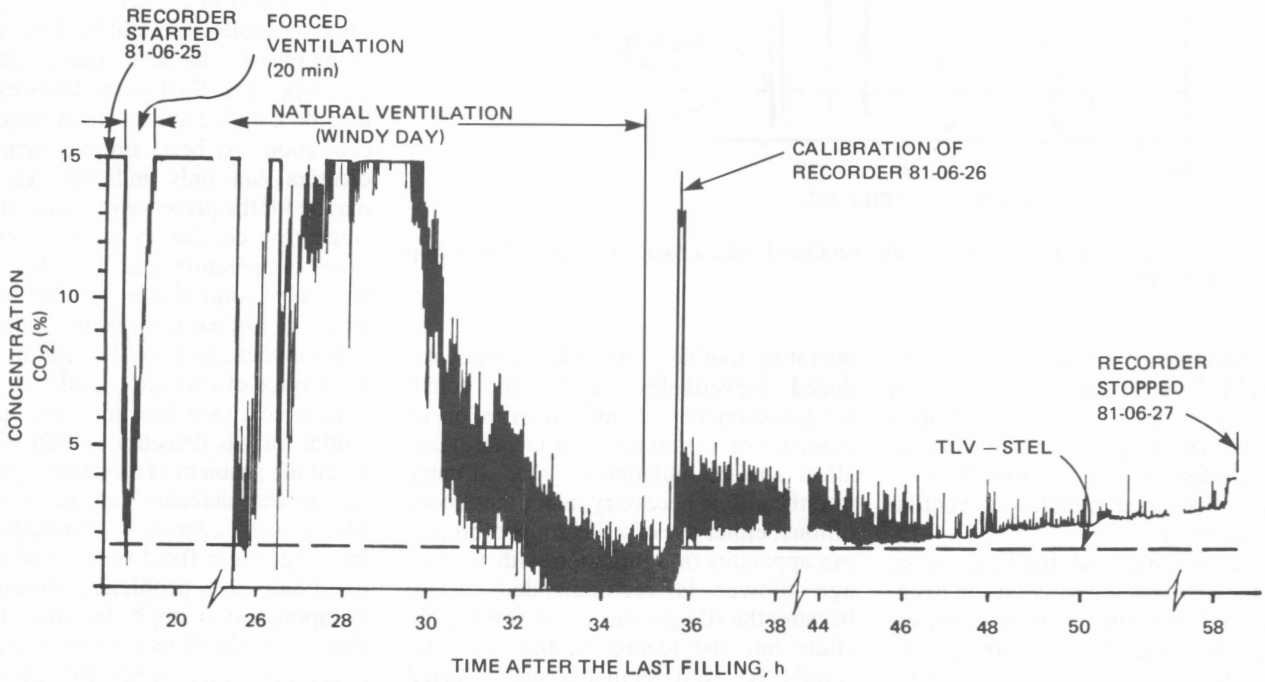

Figure 7. Recorder chart for CO_2, silo 23, 1981.

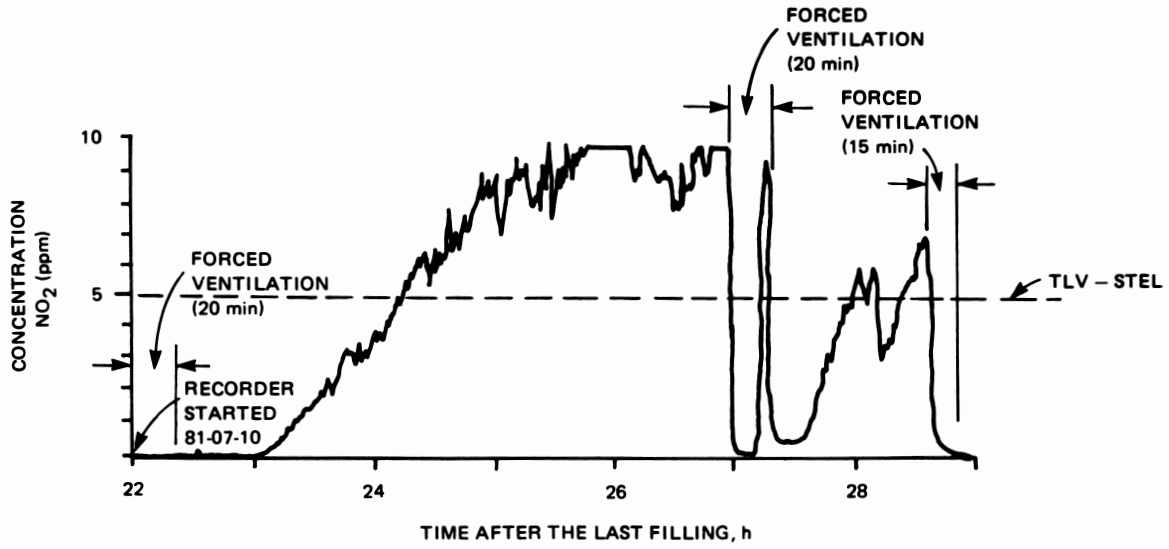

Figure 8. Recorder chart for NO_2 in silo 26, ventilated with a forage blower and 5-m drop tube, 1981.

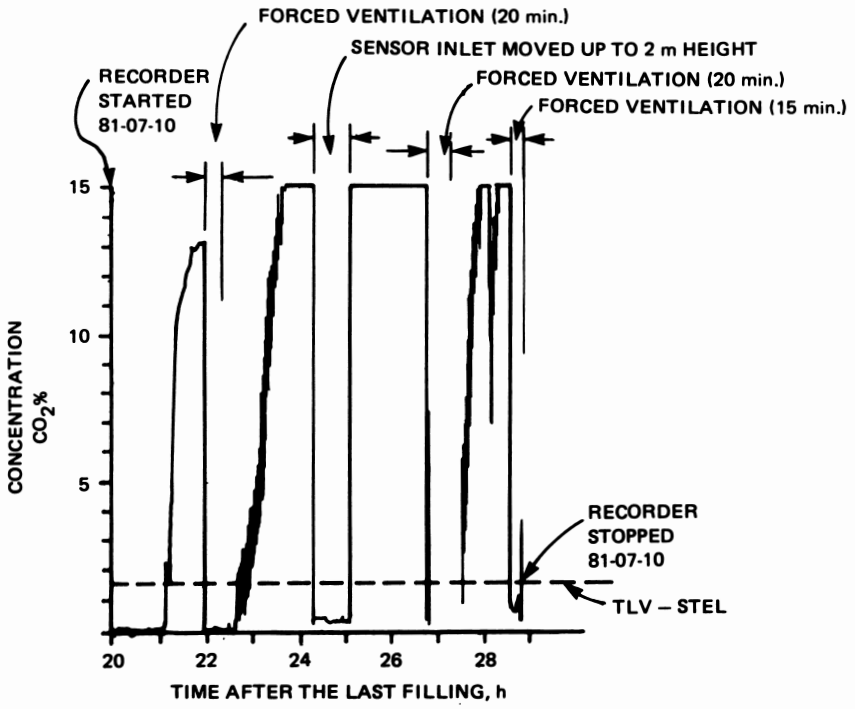

Figure 9. Recorder chart for CO_2 in silo 26, ventilated with a forage blower and 5-m drop tube, 1981.

being detectable in 1 h and reaching the TLV-STEL level in 2 h. Also of interest is the abrupt 'spike' in NO_2 concentration during the second period of ventilation. The reason for this 'spike' in the NO_2 recording, after some minutes of ventilation, is not clear.

Previous research and this field survey clearly indicate that it is very unsafe to enter a silo without taking precautions, especially during the period of rapid gas release (up to a week after the last filling). Once the silo top-unloader is installed and operating routinely, the risk is greatly reduced. Nevertheless, during the active fermentation period, any interruption of unloader operation (an hour or more) can allow a reaccumulation of gases. If entry into the silo is necessary under these conditions, either use of a life-support breathing apparatus or ventilation with the forage blower is recommended. Also, because the silo gas can spill down the silo chute into the feedroom, the feedroom should be well-ventilated and isolated from the connecting stable.

GAS DETECTORS

Existing Detectors

For detection of the hazardous gases in silos, the agricultural industry needs a low-cost, simple, reliable, accurate, easy-to-use instrument capable of taking remote readings for CO_2, NO and NO_2 up to 20 or 30 m from the operator. Silo operators, without either a suitable detector or life support equipment, enter silos at great risk. The use of unreliable indicators (such as a live rat suspended in a cage) can reduce, but not eliminate this risk.

One approach would be to find a low-cost chemically treated paper tape that would change color or give some visual measurement of dangerous gases present. Such an indicator could be lowered on a string into the silo headspace and retrieved for inspection. Such paper tapes exist, but they do not give a measure of the gas concentration. At best, simple chemical indicators can only indicate yes, no or maybe for the presence of a particular gas, since test conditions such as exposure time, temperature and humidity are not precisely controllable by the operator. They are limited to situations where there is no immediate hazard to life but where the dosage effects are cumulative.

Low-cost tape detectors may have potential for gas detection within silos provided the problem of unmetered gas transfer to the detector can be overcome. Mechanical agitation by spinning the tape in a cage for a fixed time could possibly overcome this problem inexpensively. Equipment cost might be lower than, or similar to, the detector tube-pump units, but tape costs are expected to be lower than those of the current detector tubes.

Recording instruments such as the Mexa (CO_2) and the Ecolyzer (NO_2) cost around $2000 each and were judged to be too costly for widespread use by individual farm operators.

Portable chemical tube detectors with sampling air-pumps are available in the $200 range from safety supply distributors. These detectors appear to be more practical for occasional use on farms. The problem is that the hand-held metering pump is calibrated with the glass tube plugged directly into the end of the pump. This direct coupling of tube and pump means an operator must enter the silo to take samples. This requires a breathing apparatus, which ideally includes a remote air supply tank, long hose, pressure-demand air regulator, and full-face mask (Wells 1980). With all this equipment and trained personnel on site, the need for the detector disappears.

One manufacturer (Dräger) offers an accessory extension tube up to 5.5 m long (Fig. 4) that makes remote detection feasible. The idea of using a longer extension tube for remote sampling seemed worth further investigation. Dräger chemical tube specifications appeared to have the gas selectivity required and they operate within the temperature and humidity ranges likely to be encountered in farm silos. Furthermore, Dräger offers a tube which measures the concentration of NO and NO_2 combined (termed NO_x). This reduces the number of gases to be tested to two (CO_2 and NO_x) and presents the data on the 'safe' side.

Laboratory Procedures with Chemical Tube Detectors

A preliminary laboratory investigation was done to study the suitability of four gas detectors approved by NIOSH (National Institute for Occupational Safety and Health, Morgantown, W.V. 26505), with various arrangements of pump, extension tube, chemical detector tube, and plastic bag of CO_2 test gas. The four detectors evaluated were as follows:

(1) Dräger; Drägerwerk, Postf. 1339, Moislinger Allee 53/55, D-2400 Lübec 1, West Germany (from Safety Supply Canada, 214 King St. E., Toronto, Ont. M5A 1J8).

(2) Gastec; 2-23-10 Higashi, Shibuya-Ku, Tokyo 150, Japan (from Levitt-Safety Ltd., 33 Laird Dr., Toronto, Ont. M4G 3S9).

(3) MSA; Mine Safety Appliances Co., 600 Penn Center Blvd., Pittsburgh, Pa. 15235, U.S.A.

(4) Kitagawa; (from Matheson Gas Products, 1275 Valley Brook Ave., Lyndhurst, N.J. 07071, U.S.A.).

The Dräger detector (Fig. 4) uses a rubber bellows pump squeezed by one hand, with gas flow rate controlled by the flow restriction developed by the detector tube. The other three pumps each have a cylinder and piston somewhat like an oversized hypodermic syringe (Fig. 3). Gastec (like Dräger) controls gas flow within the detector tube; MSA and Kitagawa have flow control orifices in the pump body. Tubes and pumps were used as recommended by the manufacturer for the standard configuration. The pump-tube detector system operates by drawing a known volume of gas at a controlled rate through the detector tube. The chemical in the tube changes color forming a demarcation line at a point along the tube indicating the gas concentration. The controlled gas flow rate in the tube ensures that the chemical reacts sequentially with the gas thereby giving a clear color demarcation band. Detector tubes were selected as appropriate for the test gas concentration. Five to ten tests (glass tubes) were completed and the mean calculated for each test arrangement (Table IV).

Rigorous statistical sampling procedures are used by NIOSH technicians for tube certification and for occupational exposure measurement (Hearl and Roder 1975; Roder and Ridgik 1978; Leidel et al. 1977). For example, three NIOSH technicians read each tube. For these tests, only one operator read each tube. The mean concentration was estimated between the palest and darkest coloration, interpolating to not less that 0.2 of a division. Prior to and during a test series, where practical, tests were carried out to verify that there were no leaks in the pump and test circuit. Pump delivery was verified and calculations were performed to confirm the volume within the extension tubes.

The 'standard' CO_2 concentrations in the two test gas supply cylinders were confirmed by gas chromatography at 0.105% and 0.458% by volume. These concentrations were chosen because they were read-

TABLE IV. GAS CONCENTRATION (MEAN % ± SD), LABORATORY TESTS FOR REMOTE CO_2 DETECTION WITH CHEMICAL TUBES

	Test gas 0.105% CO_2				Test gas 0.458% CO_2
Arrangement	MSA piston pump; tube no. 85976	Kitigawa pump; tube no. 8014-126A	Gastec pump; tube no. 10439	Dräger bellows pump; tube no. Ch23501	Dräger pump; tube no. CH23501
1. Pump-detector-bag	0.086 ± 0.010	0.100 ± 0.000	0.094 ± 0.010	0.084 ± 0.005	0.407 ± 0.007
2. Pump-detector-15 m extension-bag	0.094 ± 0.003	0.100 ± 0.000	0.080 ± 0.000	0.080 ± 0.003	
3. Pump-detector-30 m extension-bag	0.086 ± 0.007	0.100 ± 0.000	0.060 ± 0.000	0.079 ± 0.003	
4. Pump-15 m extension-detector-bag	Pumped 500 mL	Pumped 100 mL	Pumped 100 mL	Pumped 500 mL	Pumped 500 mL
	0.08 ± 0.000	0.059 ± 0.003	0.06 ± 0.000	0.06 ± 0.000	0.309 ± 0.013
				Pumped 1000 mL	Pumped 1000 mL
				0.099 ± 0.002	0.462 ± 0.013
5. Pump-30 m extension-detector-bag				Pumped 500 mL	
				0.058 ± 0.004	
				1000 mL	
				0.0765 ± 0.002	
				1300 mL	
				0.090 ± 0.000	
				1500 mL	
				0.099 ± 0.002	

ily available and if these concentrations could be detected reliably then higher concentrations would be even easier to detect. To fully flush out air, a 20-L collapsible 'Tedlar' plastic bag for the test gas was filled and emptied several times with the 'standard' CO_2 mixtures. Each test sample was extracted from the test bag through an internal Y-tube drawing from two points in the bag. Time intervals between samplings were kept short to minimize the possibility of CO_2 stratification within the bag. Furthermore for each pump-extension-tube arrangement, a new 'standard' (close-coupled) test was repeated to ensure that the reservoir gas had remained as specified. Five laboratory test arrangements were used as follows:

(1) pump, detector tube, gas bag ('Tedlar' plastic);

(2) pump, detector tube, 15-m extension, gas bag;

(3) pump, detector tube, 30-m extension, gas bag;

(4) pump, 15-m extension, detector tube, gas bag;

(5) pump, 30-m extension, detector tube, gas bag.

Arrangement (1) was the experimental control for comparison of the test techniques with NIOSH standards. Connections were kept closed by a pinch valve until each detector tube was inserted, then the pinch valve was reclosed after drawing each sample, repeating the procedure until all replicates were drawn.

Arrangement (2) used a 15-m extension tube of PVC plastic ('Tygon'), 6-mm inside diameter, inserted between the gas bag and pump. Preliminary tests were done with the extension tube purged 1.0, 1.25 and 1.5 and two tube volumes, to establish an acceptable purge volume. The 0.46-L extension tube was purged just over two tube volumes by pumping 10 strokes (1.0 L). The tube was then closed with a pinch valve, and the pump removed. The detector tube was then inserted between the extension tube and pump, and the sample taken after releasing the pinch valve. Subsequent tubes were inserted and samples were then taken without repurging.

Arrangement (3) was identical to arrangement 2, except that the extension length was 30 m. To maintain purging at two volumes of the extension tube, the pumps were given 20 strokes of 100 mL each.

Arrangement (4) used a detector tube coupled directly to the gas bag, with the 15-m extension tube connected between detector tube outlet and pump inlet. This arrangement is similar to the 5.5-m extension arrangement sold by Dräger. It eliminates the need for purging the extension tube, but an undetermined number of extra pump strokes is required to overcome pumping losses within the extension tube. The recommended dwell time between pump strokes was also doubled in all cases to give the test gas an opportunity to fill the pump after each stroke. For the MSA, Gastec and Kitagawa units, dwell times were based on each detector tube sensitivity and pump. For example, the MSA tube 85976 for CO_2 (0.02–12.0% range) needs five strokes at 100 sec/stroke. Doubling this requires 100 sec or 17 min. The Kitagawa tube 8014-126A needs only one stroke, but dwell time is 5 min/stroke times two, that is 10 min. The Gastec tube 10439-2LL is similar, needing only one 3-min stroke, or a dwell time of 6 min. For the Dräger unit, the pump and tube dwell time was that necessary for the stroke-limit chain to tighten, requiring 15–25 sec/stroke, or about 100 sec for the five strokes. Doubling this gives 200 sec (3.3 min), a much shorter time than any of the others.

Arrangement (5) was similar to arrangement (4), except that the extension length was doubled to 30 m, and the time between pump strokes was increased to four times that recommended, again to permit the pump to fill. Only the Dräger was tested, because the resultant test times for the other pumps would be too long. Tests were conducted with 5, 10, 13 and 15 pump strokes, theoretically giving purging volumes of 0.54, 1.09, 1.41 and 1.63 times the tube volume (the latter two with the 0.105% CO_2 test gas only).

Field Tests, Dräger Tubes vs. Mexa CO_2 Recorder

Based on the above laboratory tests and the chemical tube manufacturers' specifications, only the Dräger system was selected for field testing. Remote tube arrangements (2) and (4) appeared most promising in the laboratory and were therefore used in the field. Procedures were similar to those used in the laboratory, but without the gas bag. Arrangement (2) (15-m Teflon extension, to detector tube, to pump) and arrangement (4) (detector tube, to 15-m Tygon extension, to pump) were compared with the Mexa 221 recorder for CO_2, and with arrangement (1) (pump and tube close-coupled) for CO_2, NO_x, and NO_2. A Teflon extension tube was used with arrangement (2) to avoid absorption of NO_2 by the tubing wall.

Prior to detector tube testing a Mexa CO_2 recorder was installed in the test silo with its gas inlet located 0.3 m above the lowest point of the silage surface. For each pump-and-tube arrangement, one to four tests for CO_2, NO_x, and NO_2 were taken in each of seven silos. The technician stood in the safety cage outside the roof opening of each silo and dropped the end of the 15-m extension tubing (arrangements 2 and 4) onto the silage surface, as close as possible to the lowest point. Precise location of the sampling point was desirable but not practical. After this remote sampling, he put on his respirator, entered the silo, and took direct samples using close-coupled tube and pump arrangement 1.

Laboratory Results, Chemical Tube Detectors

Arrangement (1) All four detectors read within or close to NIOSH standards for detector tube operation, with Dräger and MSA reading somewhat lower than the others (Table IV). Repeatability of each brand of detector was good for this class of detector. The Dräger system was the most convenient to use, requiring the shortest sampling time.

Arrangement (2) All detectors again read within or close to NIOSH standards, when the extension tube was purged twice, with Dräger and Gastec reading somewhat lower than the others (Table IV). It was normal for Dräger to read a little low, even in NIOSH certification testing (Anonymous 1978). Even purging only once gave remarkably good results except for MSA which did not reach the calibration standard reading until double purging was carried out (Fig. 10). For all pumps tested, the first reading (the most similar to practical field procedures) is different, because unlike the second and subsequent readings it was preceded by a purging of the extension tube. This is illustrated by the MSA equipment when purged 1.0, 1.25 and 1.5 times (Fig. 10). Since there were no major differences between the first test reading (after double purging) and subsequent readings (without further purging), all results were grouped together for analysis.

Pumping twice the volume of the extension prior to testing achieved satisfactory purging of the 15-m extension tube. Use of the PVC extension tubing is satisfactory for CO_2 but it may give low readings for NO_2, since NO_2 may be absorbed by the plastic in sufficient quantities to reduce the readings significantly. With this arrangement, much more costly tubing (Teflon, for example) may be required for NO_x and NO_2 tests.

Arrangement (3) As with the shorter ex-

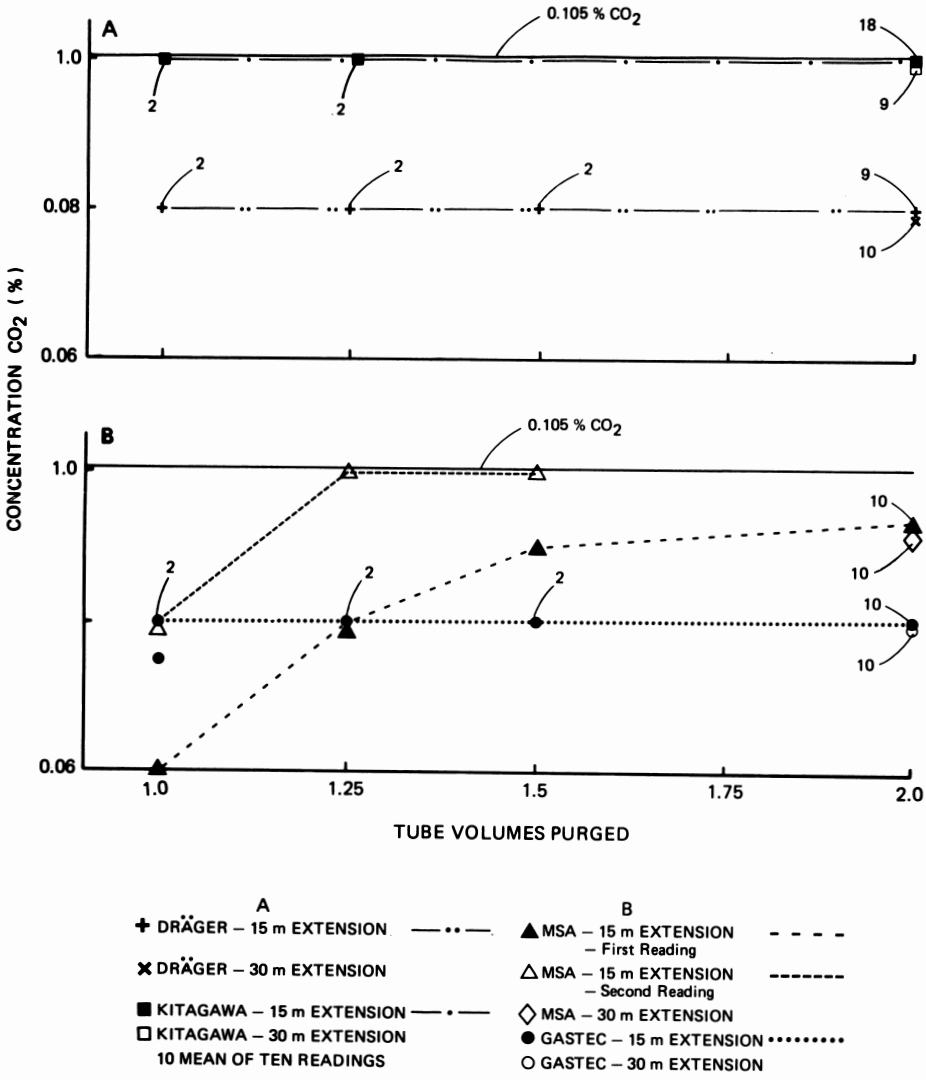

Figure 10. Effect of purge volume on remote detector accuracy. The test configuration was pump, detector tube, extension (15 or 30 m).

tension tube, purging the 30-m extension with two volumes of test gas was adequate to give readings within or close to NIOSH standards (Table IV). Again, as in arrangement (2), the first test was treated similarly to subsequent tests and grouped with them for analysis.

Arrangement (4) At 10 strokes (twice that recommended for a close-coupled test) the Dräger read to within NIOSH tolerances for both test gas concentrations (Fig. 11). This procedure was not standard, and the number of strokes was arbitrarily chosen. For the other pumps the dwell time allowed for each stroke was also doubled to compensate for the reduced flow rate through the extension tubes (Kitagawa, 10 min; Gastec, 6 min; MSA, 17 min). In consequence, only Dräger was tested at twice the recommended strokes because the other pumps required excessive test times.

Arrangement (5) At least 13 strokes (and preferably 15 strokes) were required to obtain readings within NIOSH tolerances. This test is inconclusive, and the technique requires further development before it can be considered acceptable.

At this time, neither experimental extension tube location, whether between the detector tube and the sample (arrangements 2 and 3), or between the pump and the detector tube (arrangements 4 and 5) is acceptable. Arrangements (2) and (3) look promising, but no tests with oxides of nitrogen gas have been completed to verify the acceptability of any extension tube material. Arrangements (4) and (5) are much more empirical and therefore need further testing with CO_2 and NO_x to confirm their suitability, especially at gas concentration close to the TLV-TWA and TLV-STEL levels.

Field Results, Dräger Tubes vs. Mexa CO_2 Recorder

Only very general observations can be made from the results shown in Table V, because sampling points were not identical, either within the Dräger tests or between the Mexa and Dräger tests. Where comparable readings were taken, they were of the same magnitude, but were more variable and outside the NIOSH limits for tube certification. Contrary to expectations from the laboratory studies, the CO_2 concentrations indicated by arrangements (2) and (4) (at the silage surface) were often lower than either the standard method (arrangement (1)) or the recorder, both of which were taken at 0.3 m above the surface. This indicates probable errors in these methods and reflects the difficulties encountered in correctly placing the extension tube. However, some divergence both in magnitude and variability from NIOSH standards is not surprising in the variable conditions of a real silo.

In retrospect it would have been better procedure to standardize all the sampling at one fixed height (say 0.3 m) above the low point on the silage surface. Other problems were the high cost of the Teflon extension tubing, and its stiffness which made it difficult to use. Further work is needed to find a more suitable extension tube material for NO_x testing by arrangements (2) and (3).

SUMMARY

Silage gas is a well-known hazard to silo operators and has caused a number of multiple deaths in silos. The principal hazardous gases associated with silage production are CO_2, NO, and NO_2. Nitrous oxide (N_2O) is also produced in significant quantities but it poses little risk.

Of 39 silos surveyed in Quebec, 24 showed detectable levels of the silo gases. Of these, eight silos contained one or more of these gases at concentrations above the TLV-STEL levels set by NIOSH. Gas production was observed as soon as 1 h after filling the silo and gas could persist up to at least 100 h after filling. Concentrations reached at least 150 000 ppm CO_2, 20 ppm NO, and 10 ppm NO_2. Under windy conditions, rapid changes of CO_2 concentration occurred within the silo headspace. Seven of the silos sampled after the 3-wk danger period were found to be safe; this is probably due to natural ventilation by wind, in combination with reduced gas production.

For gas detection, pumps and detector tubes from four manufacturers were tested in the laboratory, first without extension tubes, then with 15-m and 30-m extensions. The extension tubes were located either between the detector tube and pump or ahead of the detector tube. None of these detector systems can be recom-

TABLE V. IN-SILO GAS CONCENTRATIONS (%) MEASURED WITH CLOSE- AND REMOTE-COUPLED DRÄGER TUBES, AND AN INFRA-RED CO_2 ANALYZER (MEXA 221)

Gas	Silo no.	Mexa† recorder	Dräger‡ chemical tube gas detector		
			Arrangement (1)	Arrangement (2)	Arrangement (4)
CO_2	27	6.0	6.0	–	4.25 (1 stroke)
	29	0.1	0.1	0.1	–
	32	0.2	–	0.10	–
		0.2	–	0.28	–
	38	4.5	–	–	5.2 (2 strokes)
		0.2	0.3	–	0.3 (10 strokes)
		3.5	–	2.6	–
		3.0	–	2.5	–
		1.5	1.25	–	–
		0.5	–	0.5	–
	39	3.8	–	2.5	
		3.6	–	2.5	2.9 (10 strokes)
		4.5	3.5	3.5	–
		0.8	–	0.5	–
	40	7.0	–	5.0	–
		2.0	–	–	1.6 (2 strokes)
		2.9	–	1.1	–
		0.4	–	–	0.4 (10 strokes)
		0.2	–	0.15	–
		0.1	–	0.7	–
NO_2§	35	–	–	3 ppm	
NO_x§	35	–	–	17 ppm	4 ppm

†Mexa 221 samples taken at 0.3 m above the lowest point of the silage surface.
‡Dräger samples were taken at the silage surface as near as possible to the lowest point.
§Teflon extension tube used for NO_2 and NO_x measurements.

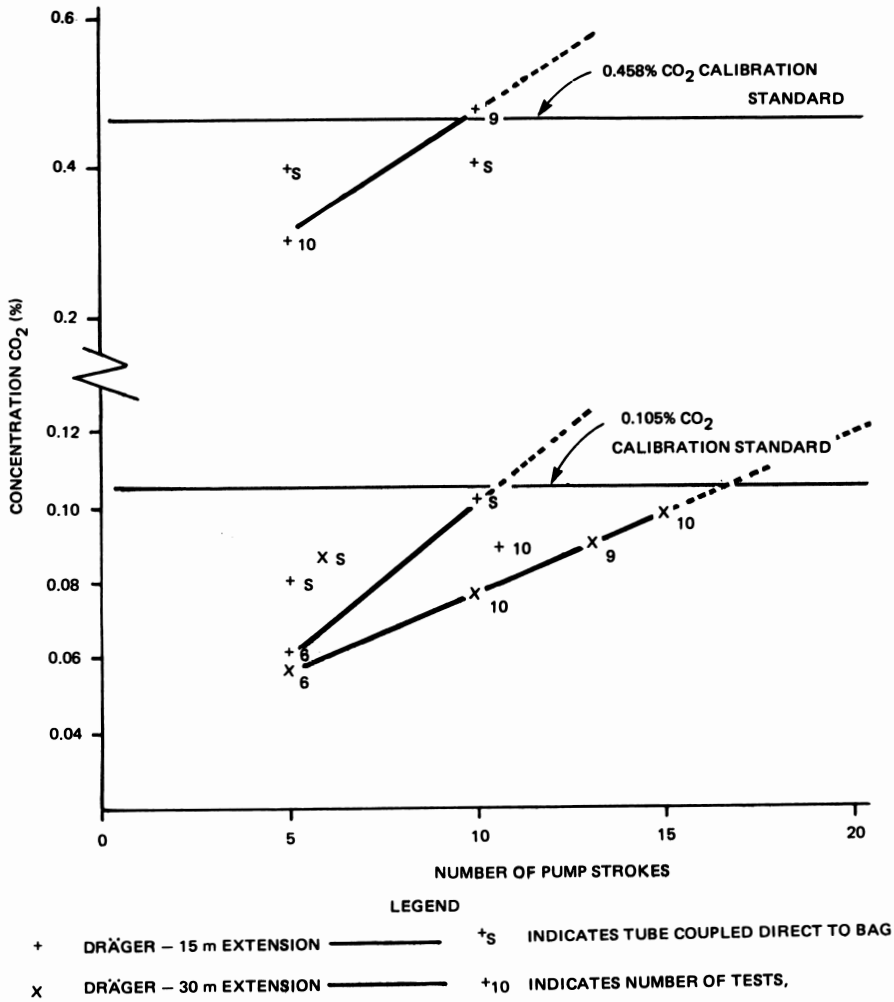

Figure 11. Effect of number of pump strokes on detector accuracy. The test configuration was pump, extension (15 or 30 m), detector tube.

mended until more tests with CO_2 and new tests with oxides of nitrogen and other more suitable extension tube materials can be completed. The Dräger pump was the easiest to operate and employs detector tubes covering the temperature and humidity ranges likely to be found in silos. Field tests demonstrated the practicality of this approach but there is a need to establish an acceptable sampling height and technique to determine sampling location. Only the Dräger system with an extension tube was tested in the silo because it was the only system capable of completing a test in an acceptable time. More development is needed in techniques of remote gas detection in silos.

REFERENCES

ANONYMOUS 1980. TLV's, threshold limit values for chemical substances and physical agents in the workroom environment, with intended changes for 1980. Am. Conf. of Govt. Ind. Hygienists, Airborne Contaminants Committee, P.O. Box 1937, Cincinnati, Ohio.

ANONYMOUS 1978. Gas detector tube performance testing summary, investigation no. 84-06-3-040-004. National Inst. of Safety and Health (NIOSH), U.S. Dep. of Health, Education and Welfare, Chestnut Ridge Rd., Morgantown, W.V.

ANONYMOUS 1977. Occupational diseases, a guide to their recognition. National Inst. of Safety and Health (NIOSH), Dep. of Health, Education and Welfare, Chestnut Ridge Rd., Morgantown, W.V. pp. 415–417.

COMMINS, B.T., F.J. RAVENEY, and J.W. JESSON. 1971. Toxic gases in tower silos. Ann. Occup. Hyg. 14: 275–283.

DELANEY, L.T., H.W. SCHMIDT, and C.F. STROEBEL. 1956. Silo-fillers disease. Mayo Clin. Proc. 31: 189–198.

DUBRUNFAUT, M. 1868. Mémoirs présentés sur la distillation des betteraves et la fermentation dit nitreuse. C.R. Acad. Sci. 66: 275–277.

GRAYSON, R.R. 1956. Silage gas poisoning: nitrogen dioxide pneumonia, a new disease in agricultural workers. Ann. Intern. Med. 45: 393–408.

HAYHURST, E.R. and E. SCOTT. 1914. Four cases of sudden death in a silo. J. Am. Med. Assoc. 63: 1570–1572.

HEARL, F.J. and M.M. RODER. 1975. Test procedure for gas detector tube certification. NIOSH/TC/A-001. National Inst. for Occup. Safety and Health, Morgantown, W.V.

HORVATH, E.P., G.A. DO PICO, R.A. BARBEE, and H.A. DICKIE. 1978. Nitrogen dioxide — induced pulmonary disease — five new cases and a review of the literature. J. Occup. Med. 20(2) 103–110.

KENNEDY, M.C.S. 1972. Nitrous fumes and coal-miners with emphysema. Ann. Occup. Hyg. 15: 285–301.

KOSMIDER, S., K. LUDYGA, A. MISIEWICZ, et al. 1972. Experimental and clin-

ical investigations of the emphysematous effects of nitrogen oxides. Zentralbl. Arbeitsmed. 22: 362–368.

LEIDEL, N.A., K.A. BUSCH, and J.R. LYNCH. 1977. Occupational exposure sampling strategy manual. DHEW(NIOSH) Pub. No. 77-173, National Inst. For Occup. Safety and Health, Morgantown, W.V.

LOWRY, T. and L.M. SCHUMAN. 1956. Silo-fillers disease — a syndrome caused by nitrogen dioxide. J. Am. Med. Assoc. 162: 153–160.

NICHOLS, B.H. 1930. The clinical effect of the inhalation of nitrogen dioxide. Am. J. Roentgen. 23: 516.

PARTINGTON, J.R. 1957. A textbook of inorganic chemistry. 6th ed. MacMillan and Co. Ltd., London. 537 pp.

PETERSON, W.H., R.W. THOMAS, and R.F. ANDERSON. 1949. Yellow gas from corn silage. Hoards Dairyman 94: 870–871.

PETERSON, W.H., R.H. BURRIS, R. SANT, and H.N. LITTLE. 1958. Production of toxic gas (nitrogen oxides) in silage making. J. Agric. Food Chem. 6(2): 121–126.

RODER, M.M. and T.A. RIDGIK. 1978. NIOSH certification requirements for gas detector tube units. NIOSH/TC/A-012, National Inst. for Occup. Safety and Health, Morgantown, W.V.

SABOURIN, H.M. 1983. Production, détection et évaluation des gaz toxiques (CO_2 et NO_x) dans les silos verticaux. Agriculture Canada, contract report no. 35SZ.01843-0-ME09, Ottawa, Ont.

SCALETTI, J.V., C.E. GALES, R.A. BRIGGS, and L.M. SCHUMAN. 1960. Nitrogen dioxide production from silage: I, field survey. Agron. J. 52(7): 369–372.

SCALETTI, J.V., J.J. GAZESKI, J.J. GATES, and L.M. SCHUMAN. 1965. Nitrogen dioxide production from silage: II, detailed field study. Agron. J. 57(1): 65–67.

SCHROTTMAIER, J. 1982. Protection from silo gas. Ergonomics 25(1): 89–105 Jan.

VAN OETTIGEN, W.F. 1941. The toxicity and potential dangers of nitrous fumes. U.S. Public Health Service Bul. 272. Supt. of Documents, Govt. Printing Office, Washington, D.C.

VIGDORTSCHIK, N.A., E.C. ANDREEVA, I.Z. MATUSSEVITSCH, et al. 1937. The symptomatology of chronic poisoning with oxides of nitrogen. J. Indust. Hyg. Toxicol. 19: 469–473.

WANG, C.L. and R.H. BURRIS. 1960. Mass spectrometric study of nitrogenous gases produced by silage. J. Agric. Food Chem. 8(3): 239–242.

WELLS, D. 1980. Respiratory protection for agricultural tower silos and manure pits. Farm Safety Assoc. Inc., 340 Woodlawn Rd., Guelph, Ont.

WHITTENBURY, R., P. McDONALD, and D.G. BRYAN-JONES. 1967. A short review of some biochemical and microbiological aspects of ensilage. J. Sci. Food Agric. 18: 441–444.