INSTRUMENTAL METHODS FOR THE DETECTION OF HIGHER OXIDES OF NITROGEN IN NITROUS OXIDE

BY

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SUMMARY

This paper discusses the possible application of instrumental methods used by the British Coal Utilisation Research Association for flue gas analysis to detect the contamination, by higher oxides of nitrogen, of nitrous oxide (N\textsubscript{2}O) intended for use as an anaesthetic. Two galvanic instruments sensitive to 1 p.p.m. v/v of nitrogen dioxide (NO\textsubscript{2})—or, when supplemented by a pre-oxidizer, of nitric oxide and nitrogen dioxide (NO + NO\textsubscript{2})—are described; either might be adapted to actuate an alarm. The methods are discussed in the light of governmental standards of air quality.

The possibility of contamination of nitrous oxide by higher oxides of nitrogen may make it desirable for the clinician to have his own means for the routine testing of N\textsubscript{2}O.

In considering the highest concentrations of toxic substances in air that will probably not have ill effects on healthy people, the American Conference of Governmental Industrial Hygienists has adopted, in its annually revised Table of Threshold Limit Values, a TLV of 5 p.p.m. v/v for NO\textsubscript{2}. No limit for NO is included, presumably because this would be expected to be oxidized to NO\textsubscript{3}. The limit of 5 p.p.m. v/v for NO\textsubscript{2} is accepted in the United Kingdom by H.M. Factory Inspectorate (1966) and for the present purpose a value of not higher than 5 p.p.m. v/v of (NO + NO\textsubscript{2}) will be assumed as the concentration to which detectors must give an appreciable response if they are to be useful to monitor anaesthetic gases.

Considerable experience has been gained by the BCURA of the use of two instruments, the Hersch sensor and the Mast meter, for the determination of higher oxides of nitrogen in flue gas and the opportunity was taken to ascertain whether these instruments would be suitable for the routine monitoring of N\textsubscript{2}O. Both were found capable of detecting as little as 1 p.p.m. v/v of NO\textsubscript{2} or, if used in conjunction with an oxidizer, of (NO + NO\textsubscript{2}), in nitrous oxide.

THE HERSCH SENSOR

The Hersch sensor (Hersch and Deuringer, 1963a) is a fuel cell. A simple form of the device, having no moving parts, is shown in figure 1. The cathode consists of two layers of platinum gauze with a glass fibre filter-paper between them which acts as a wick to keep the cathode moistened by the electrolyte, a neutral buffered solution containing 3 mole/litre KCl, 0.1 mole/litre KH\textsubscript{2}PO\textsubscript{4} and 0.1 mole/litre K\textsubscript{3}HPO\textsubscript{4}. The anode consists of activated carbon powder enclosed in an envelope of graphite cloth, and a plug of glass wool prevents carbon particles that may become detached from the anode from floating up to the cathode. The circuit may be completed through an external microammeter, or a resistance in parallel with a voltage recorder may be used to provide a permanent record, or again the sensor may be made to actuate a simple form of alarm.

![Hersch sensor to modified design.](https://academic.oup.com/bja/article-abstract/40/4/299/315686)
When NO₂ enters the sensor, some of it is galvanically reduced at the moistened platinum cathode, in accordance with the equation:

\[ \text{NO}_2 + \text{H}_2\text{O} + 2e = \text{NO} + 2\text{H}^+ \]

The hydroxyl radicals migrate through the electrolyte and are discharged at the anode:

\[ \ldots \ldots \text{C} + 2\text{H}^+ = \ldots \ldots \text{CO} + \text{H}_2\text{O} + 2e \]

(\ldots \ldots \text{C} \text{ and } \ldots \ldots \text{CO} \text{ represent different states of oxidation of the active carbon}). The electrons return to the cathode via the external circuit.

Not all the NO₂ entering the sensor reacts in this way; some escapes, and some reacts non-galvanically in accordance with the equation:

\[ 3 \text{NO}_2 + \text{H}_2\text{O} = 2 \text{HNO}_3 + \text{NO} \]

Of the NO₂ entering the sensor, the proportion that reacts galvanically is influenced by the concentration of the NO₂, by the rate of flow of the gas stream, by the temperature and by the geometry of the sensor. Hence each sensor needs to be calibrated; a method for generating known concentrations of NO₂ for this purpose has been given by Shaw (1967), after Hersch and Deuringer (1963b).

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**Fig. 2**

Influence of concentration of NO₂ on the electrical output from a typical Hersch sensor at constant temperature (29°C) but various rates of flow of carrier gas.

Figures 2, 3 and 4 illustrate the influence of concentration of NO₂, rate of flow of carrier gas, and temperature on the output of a typical sensor. If, at a given temperature, the mass flow rate of NO₂ into the sensor is low, then the signal is directly proportional to the flow rate of carrier gas as well as the concentration of NO₂; if, however, the mass flow rate of NO₂ is sufficiently high, the
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signal becomes almost independent of the flow rate, which therefore need not be closely controlled. For work of the highest accuracy the sensor must be used at constant temperature but this is unnecessary where a pass/fail indication at an amply safe level is all that is required, or if the apparatus is used in efficiently air-conditioned premises. The sensor can readily be made to withstand the pressures prevailing in anaesthetic apparatus.

If in constant use, the sensor should be refilled daily with fresh electrolyte.

The sensor will give an electrical response to other substances that can be galvanically reduced or oxidized by the electrode system. It responds strongly to SO$_3$ and HNO$_3$, which are reduced, and it responds strongly but with reversed polarity to NH$_3$, H$_2$S and SO$_2$ which are oxidized. The sulphur compounds tend to poison the sensor, reducing its subsequent sensitivity towards NO$_3$, but these gases are unlikely to be encountered in cylinder N$_2$O.

Table I contrasts the signal obtained from a 100 p.p.m. v/v concentration of NO$_3$ in nitrogen at 15°C and a flow rate of 100 ml/min with the signals obtained from the same concentration and flow rate of CO, H$_3$ and SO$_2$; the effectiveness of the sensor as an NO$_3$ meter is clearly seen.

No signal could be detected when nitric oxide or nitrous oxide at high concentrations in nitrogen were passed through the sensor. Therefore, in order to obtain a signal from any NO that may be present in N$_2$O, an oxidizer unit that will convert NO to NO$_3$ but leave N$_2$O untouched must precede the sensor. A suitable oxidizer unit is described below. Of crucial interest are the observations that 100 per cent N$_2$O caused no detectable output from the sensor, but that a strong response was obtained when 5 p.p.m. v/v of NO$_3$ were added to the N$_2$O. As far as is known, the Hersch sensor is not commercially available, but the modified design shown in figure 1 has been made at the BCURA laboratories at a direct cost (materials and labour) of about £10, to which perhaps £20 should be added to cover the cost of a flowmeter and microammeter.

**THE MAST METER**

The Mast meter (fig. 5) is an adaptation of the Oxford-Kew ozone sonde (Brewer and Milford, 1960). Like the Hersch NO$_3$ sensor, it responds to any substance capable of giving rise to a galvanic reaction in its electrochemical system.

<table>
<thead>
<tr>
<th>Feed gas: 100 ml/min of N$_2$ containing 100 p.p.m. v/v of named gas</th>
<th>CO</th>
<th>H$_3$</th>
<th>SO$_2$</th>
<th>NO$_3$</th>
<th>N$_2$O</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal from Hersch sensor (µA)</td>
<td>0.1</td>
<td>1.3</td>
<td>32</td>
<td>160</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
</tbody>
</table>
oxidant such as NO₂, present in the sample gas reacts with the electrolyte to form iodine which combines with the hydrogen on the cathode, thus tending to depolarize the system. In order to restore the hydrogen layer an electric current flows through the external circuit, and the magnitude of this current is a measure of the concentration of oxidant in the gas entering the meter. The meter, already calibrated ready for use, is available commercially. This instrument also is unaffected by N₃O.

The Mast instrument is much more sensitive to ozone, chlorine and iodine vapour than to NO₂, but again these gases that would interfere with the determination of NO₂ are unlikely to occur in N₂O.

Like the Hersch sensor the Mast instrument does not respond to NO; an oxidizer must therefore be included in the gas line to the instrument. Unlike the Hersch sensor, the Mast instrument contains delicate pumps and must therefore be used at atmospheric pressure. The Mast instrument is commercially available from the Mast Development Company of Davenport, Iowa, U.S.A. Without recorder, its cost in 1967 was $1017 exclusive of import duty.

APPLICATION TO ANAESTHETIC N₂O

While the Hersch sensor or the Mast instrument could conveniently be incorporated in an anaesthetic apparatus at the clinic, it would appear that their installation at manufacturers' works would afford adequate protection at trifling cost, provided that the N₂O can be guaranteed not to deteriorate under any conditions to which the cylinders may be exposed after filling.

OXIDIZER FOR NO

A suitable oxidizer unit for converting NO to NO₃ in the presence of N₂O (which remains unchanged) consists of a glass tube about 6 cm long by 8 mm internal diameter containing 1–2 g of glass wool impregnated with chromium trioxide and sulphuric acid (Bethell, Shaw and Thomas, 1968). The oxidant is prepared by soaking glass wool in an aqueous solution containing 15 g each of K₂Cr₂O₇ (laboratory reagent grade) and H₂SO₄ (98 per cent analytical grade) in 100 ml. After excess solution has been drained off, the glass wool is heated at 60–65°C in air for 18 hours. About 1.5 g of reagent is retained per g of glass wool. Before use the oxidant is kept at 25°C for 30 minutes in a constant temperature enclosure containing a beaker of water, as the efficiency is found to be best if the oxidant is slightly moist.

For use with the Mast or Hersch instruments this oxidant has been found superior to that described by Ripley, Clingenpeel and Hurn (1964) as it has a much longer life. For example, in a 3-hour test, in which the rate of flow of gas through the oxidizer unit was 140 ml/min the efficiency with which a 100 p.p.m. v/v concentration of NO was oxidized to NO₃ remained above 95 per cent throughout, in contrast to the life of about 10 min in such conditions claimed for the oxidizer described by Ripley and his colleagues.

The frequency with which the oxidizer should be changed will depend very much on the conditions of use. Experience has shown that if a virtually moisture-free gas (such as N₂O from a cylinder might be) is passed for a considerable time through the oxidizer unit of Bethell, Shaw and Thomas, the unit gradually loses its ability to oxidize NO, even if there has been nothing for it to oxidize. In a severe test, oxygen-free nitrogen which is virtually dry, was led for 12 hours at 150 ml/min through an oxidizer unit whose efficiency had fallen, through use, to 90 per cent. The temperature was from 14°C to 18°C. Intermittent testing by introducing NO to the nitrogen to give a concentration of about 35 p.p.m. v/v showed that the efficiency of oxidation to NO₃ fell off at a steady rate of about 2 per cent relative per hour, to reach 70 per cent after 12 hours' continuous exposure to the flow of nitrogen. The efficiency was restored to 90 per cent by merely leaving the oxidizer open to the air for 3 hours.

Because adsorption equilibrium has to be achieved, the NO₃ output from a new oxidizer, or from one that has been flushed with NO-free gas, does not immediately reach its theoretical value when a low concentration of NO appears in the gas stream, but rises gradually, the apparent efficiency of oxidation reaching a high value after a lapse of about 5 minutes.

"SHELF LIFE" OF THE OXIDIZER

Bethell, Shaw and Thomas (1968) stated that the oxidizer can be kept in a well-stoppered bottle for at least a week without loss of activity. Experi-
ence has shown this to have been a very conservative assessment, and there is no reason to suppose that the oxidizer would not keep indefinitely if put up in sealed tubes and kept in an ordinary chemical storeroom.

CONCLUSIONS
Both the Hersch and the Mast instruments are insensitive to $N_2O$ but their response to $NO_2$ is ample to detect concentrations down to 1 p.p.m. v/v, in $N_2O$. Both appear suitable for installation at manufacturers' works or at the clinic for the routine continuous monitoring of $N_2O$ for $NO_2$ or, with a pre-oxidizer, for ($NO + NO_2$).

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REFERENCES