*Journal of Chromatography, 630 (1993)* 257–263
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 722

# Ambient temperature gas purifier suitable for the trace analysis of carbon monoxide and hydrogen and the preparation of low-level carbon monoxide calibration standards in the field

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(Received August 7th, 1992)

## ABSTRACT

A novel gas purifier based upon Sofnocat 682, a catalyst containing platinum and palladium on a hydrophobic tin oxide support, is described for the quantitative removal at ambient temperatures of ppm (v/v) and sub-ppm (v/v) levels of carbon monoxide and hydrogen from air and nitrogen gas cylinders. This method provides a simple means of generating either a laboratory or field source of "zero grade" gas for both the trace analysis of carbon monoxide and hydrogen and the preparation of working calibration gas standards of carbon monoxide by using a simple one-step dilution of a higher concentration certified gas standard.

## INTRODUCTION

Of particular interest to our laboratory and many other workers [1–9] is the analysis of carbon monoxide and hydrogen at ppm (v/v) and sub-ppm (v/v) levels, particularly since carbon monoxide and hydrogen are produced and released into the atmosphere from a variety of largely anthropogenic sources, including automobiles, domestic heating and biomass burning. Carbon monoxide also plays an important role in atmospheric chemistry through its reaction with hydroxyl radicals [4,10,11].

When the analysis of carbon monoxide and hydrogen involves gas chromatography with a sensitive detector, accurate quantitation can only be achieved when the carrier gas is free from the target analyte [12–14]. Similary, where low-level calibration standards are made by successive dilution of a more concentrated certified standard, the diluent gas must also be free of the target analyte [14]. Commercial compressed gas supplies often contain levels of carbon monoxide and hydrogen in excess of their global mixing ratios. The purchase of commercial "zero grade" carrier gases is often an expensive option and, even then, is not always adequate for analyses at the sub-ppm (v/v) level [14]. Consequently, most laboratories purify their carrier gases by various methods including disposable [15] or thermally regenerable adsorbents [16], cryogenic traps [17] or catalytic removal at elevated temperatures [14,18,19]. However, because of the power constraints of heated catalysts and the logistics associated with cryogenic coolants a requirement exists in the field for a catalyst that can remove both carbon monoxide and hydrogen from either air or nitrogen carrier gas at ambient temperature and at varying levels of humidity.

The majority of catalysts used for the oxidation of carbon monoxide have been developed for high-

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0021-9673/93/$06.00

temperature automobile catalytic converters. However, for conditions of ambient or moderate temperatures ($< 100°C$) and varying levels of water, the choice of catalyst is severely restricted. Carbon monoxide can be removed by the passage of the gas over hopcalite [20], a proprietary mixture of oxides of copper and manganese, but although the hopcalite is resistant to poisoning, temperatures of $> 70°C$ are required to avoid catalyst deactivation by adsorbed water [21]. Noble metal catalysts such as palladium and/or palladium on either alumina or charcoal will oxidise carbon monoxide at ambient temperatures but the catalysts are very sensitive to poisoning [22–24]. Furthermore, those on a hydrophilic alumina base are susceptible to deactivation by water, although it is claimed that methylsilation of hydrophobic supports alleviates this problem [25]. A further class of catalysts developed for ambient carbon monoxide oxidation is based upon copper salts, usually with smaller amounts of precious metal salts such as palladium chloride [26,27]. One such catalyst, LTC 987 from Teledyne Water Pik, is used in combination with activated charcoal for the removal under ambient conditions of carbon monoxide from buildings [28,29]. However its performance has been reported to be optimum only at 20–65% humidity levels [25]. Silver oxide has also been reported by Seiler *et al.* [10], to quantitatively remove carbon monoxide at room temperature but an additional high temperature hopcalite bed is required to remove hydrogen. Iodine pentoxide exhibits similar limitations [14].

In our own studies [30] on catalysts for the removal of carbon monoxide and hydrogen at ambient temperatures and humidities within enclosed environments, we have found Sofnocat 682 to be the most efficient catalyst, particularly in terms of hydrogen removal and resistance to poisoning. Sofnocat 682 contains both platinum and palladium and a promotor, such as nickel or manganese, on a hydrophobic tin oxide support [31]. With Sofnocat 682, residence times of $<0.1$ s are required for the complete oxidation of carbon monoxide [32], this being less than the corresponding residence times for hopcalite ($> 0.8$ s) [24] and conventional precious metal catalysts (0.2-0.5 s) [23].

This paper describes the use of Sofnocat 682 catalyst operating at ambient temperature for the quantitative removal of both carbon monoxide and hydrogen from air and nitrogen gas cylinders so as to provide a field source of "zero grade" gas for both the trace analysis of carbon monoxide and hydrogen and the preparation of working calibration gas standards of carbon monoxide by using a simple one-step dilution of a higher-concentration certified gas standard.

## EXPERIMENTAL

### *Catalyst material*

Extrudates (1 mm) of Sofnocat 682 (Molecular Products, Thaxted, Essex, UK) were used as received. For laboratory studies the catalysts were contained in 316-grade stainless-steel tubes (12 in. × 1 in. O.D. × 0.040 in. wall; 1 in. = 2.54 cm) with welded 1/8-in. NPT(F) inserts into which were fitted Swagelok connectors incorporating 1/8 in. O.D. × 1.8 in. thick coarse bronze sinters ("F" grade, 160-180 $\mu$m, Accumatic Engineering, Wrexham, UK). When packed, these tubes contained 238 g of Sofnocat 682 catalyst. For subsequent field tests, Sofnocat 682 catalyst (46.9 g) was contained in a 316-grade stainless-steel tube (6 in. ×3/4 in. O.D. × 1/16 in. wall) fitted with Swagelok 1/4-in. NPT(M) fittings containing integral bronze sinters.

### *Carbon monoxide and hydrogen analyses*

Carbon monoxide and hydrogen were analysed using a RGA-2 reduction gas analyser (Trace Analytical, Menlo Park, CA, USA). This technique, pioneered by Seiler *et al.* [10], is based upon the reduction of hot mercuric oxide by carbon monoxide and hydrogen, and the photometric detection of the mercury vapour evolved. Air carrier gas (CP Grade, BOC, Wembley, UK) was supplied via a two-stage Model 11 regulator (Scott Environmental Technology, Plumsteadville, PA, USA). Using a 3 ft. ×1/4 in. O.D. 5A molecular sieve column (1 ft. = 30.48 cm) maintained at 120°C and a nominal carrier gas flow of 40 ml/min, carbon monoxide and hydrogen were separated with baseline resolution at retention times of cu. 2.0 and ca. 0.4 min, respectively. The detector was operated at 270°C. Samples were introduced onto the column using a Valco 6-port 1/16-in. low-dead-volume valve (P/N 9105, Alltech Associates, Carnforth, UK) fitted with a Valco l-ml sampling loop. The output from the detector was connected to a Hewlett-Packard 3396A reporting integrator. Quantitation of carbon monoxide levels was determined by calibration with a single Scotty IV gas standard (Scott Environmental Technology) containing 1.02 ppm (v/v) (certified accuracy ± 2%) of carbon monoxide in air. Replicate analyses ($n = 5$) at this level gave a reproducibility of $\leqslant 0.5\%$. Using other Scotty IV standards, the detector response was shown to be linear up to at least the 2 ppm (v/v) level, thereby ensuring linearity of detection for all carbon monoxide levels used in our studies. Hydrogen levels were quantified using a single Scotty IV gas standard containing 12.2 ppm (v/v) (certified accuracy ± 2%) of hydrogen in nitrogen. This concentration gave a response within the linear range of the detector.

### *Long-term tests on catalysts*

Long-term laboratory tests were performed to assess the ability of Sofnocat 682 to remove carbon monoxide and hydrogen from both air [0.327 ppm (v/v) CO, 3.00 ppm (v/v) $H_2$, CP grade, BOC] and nitrogen [0.196 ppm (v/v) CO, 0.040 ppm (v/v) $H_2$, 4.40 ppm (v/v) $O_2$, "White Spot" grade, BOC]. The test apparatus used to assess the catalytic efficiency is shown in Fig. 1. The flow through the catalyst was controlled to 50 ml/min by a Brooks Model 8744 flow controller (Brooks Instruments, Stockport, UK). Periodic measurements of the input concentrations to the catalysts were made by operating the two Whitey OGS2 toggle valves (Bristol Valve and Fitting Company, Bristol, UK) to divert the gas flow. The diverted gas flow was set to 50 ml/min via a Nupro Model SS2 metering valve. For experiments at flows above 100 ml/min the Brooks flow controller was removed and the flow adjusted via the two stage regulator on the cylinder, a pressure of 13 p.s.i.g. (1 p.s.i.g. = 6894.76 Pa) being required to achieve a flow of *ca.* 100 ml/min through the Sofnocat 682 catalyst bed. In all cases the flows were measured with either 0-100 or 0–1000 ml/min Hastings mass flowmeters (Chell Instruments, Norfolk, UK).

Following the laboratory studies, a trap containing 46.9 gm of Sofnocat 682 was used for eighteen months as the "gas purifier" for air carrier gas cylinders used on a RGA-3 reduction gas analyser (Trace Analytical, Stanford Avenue, Menlo Park, California, USA) operated as a field monitor for tropospheric CO levels. The carrier gas flow-rate was nominally 20 ml/min. For all catalyst tests, ei-

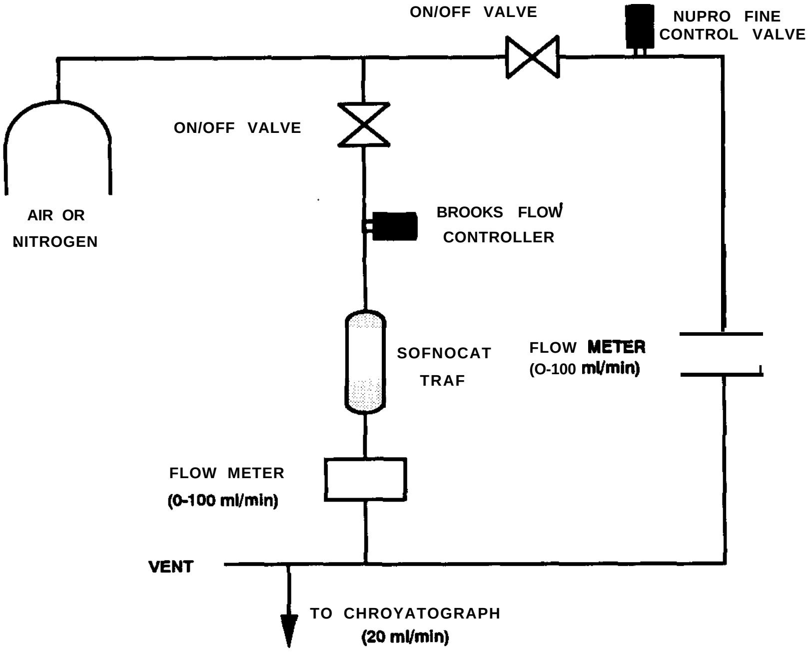

Fig. 1. Schematic diagram of the test system used to evaluate the catalyst efficiency.

ther in the laboratory or in the field, the ambient temperature was in the range 15–25°C.

### *Preparation of low-level carbon monoxide calibration standards using a one-stage dilution*

Initially, a working CO standard was prepared by dilution of a 1000 ppm (v/v) CO standard (BOC) in air. This standard was analysed using the Scotty IV standards described earlier, and found to contain 1.82 ppm (v/v) of CO. Sub-ppm (v/v) standards of carbon monoxide were prepared by a single-step dilution of the 1.82 ppm (v/v) CO standard. The apparatus used was identical to that shown in Fig. 1, other than the addition of a 6 in. × 3/4 in. O.D. stainless-steel mixing volume where the two flows are combined. Prior to performing dilutions of the gas standard, it was confirmed that the Sofnocat 682 removed >99.5% of the carbon monoxide from the CO gas standard at flows of both 100 and 950 ml/min. Dilutions of up to 100-fold were made by simply blending the undiluted and “CO scrubbed” flows from the Sofnocat 682 to maintain a combined maximum flow of 100 ml/min. The flows were accurately measured using either 0–10 or O-100 ml/min mass flow meters as appropriate. To avoid any memory effects the dilutions were performed using increasing concentrations. The diluted gas standard was split, part to the gas sampling valve, the balance being vented to avoid back pressuring the system. The quantitative removal efficiency of the Sofnocat 682 catalyst for carbon monoxide was confirmed at the end of each series of dilutions.

## RESULTS AND DISCUSSION

The Sofnocat 682 trap containing 238 g of catalyst was tested in the laboratory for the purification of air at a flow-rate of 50 ml/min for a total of 2575 h (107 days). Of this time, 1920 hours were with air containing 0.327 ppm (v/v) CO and 3.00 ppm (v/v) $H_2$, and 655 h with the gas standard containing 1.82 ppm (v/v) CO and 1.08 ppm (v/v) $H_2$. At the end of these tests, the Sofnocat 682 was still removing >99% of both carbon monoxide and hydrogen from the air carrier gas. This quantitative removal efficiency was also observed during shorter duration tests at the higher flows of 100,640 and 940 ml/min.

A similar Sofnocat 682 trap containing 246 g of catalyst was evaluated at 50 ml/min for the purification of nitrogen for a total of 2136 h (89 days). At the end of these tests, the Sofnocat 682 was still removing >99% of carbon monoxide from an input concentration of 0.196 ppm (v/v). No hydrogen breakthrough was observed from the nitrogen test gas containing 0.040 ppm (v/v) of hydrogen. Since this level is not far above the system detection limit for hydrogen, the hydrogen removal efficiency was determined on completion using a nitrogen source containing 8.1 ppm (v/v) of hydrogen and 0.345 ppm (v/v) of carbon monoxide. Quantitative (i.e. >99%) removal of both species was observed. Since the mechanism for both carbon monoxide and hydrogen removal is oxidative [33], the quantitative removal of the gases in high-purity nitrogen of nominally 8 ppm (v/v) total impurities was somewhat unexpected. We therefore assume that sufficient residual oxygen is present in the system to facilitate oxidation.

The above results therefore demonstrate the suitability of Sofnocat 682 catalyst to purify the carrier gas on ambient carbon monoxide and hydrogen analysers in which either air or nitrogen are employed as carrier gases. Analysis of a random batch of ten. commercially supplied, air gas cylinders gave carbon monoxide levels in the range 0.04440.800 ppm (v/v) [mean 0.354 ppm (v/v) S.D. ± 0.222 ppm (v/v)] and hydrogen levels of 0.87-2.76 ppm (v/v) [mean 1.43 ppm (v/v), S.D. ± 0.71 ppm (v/v)]. Analysis of four high-purity commercial nitrogen cylinders chosen at random gave carbon monoxide levels ranging from 0.07880.345 ppm (v/v) [mean 0.178 ppm (v/v), S.D. ± 0.096 ppm (v/v)], the hydrogen levels varying over the range 0.049-g. 1 ppm (v/v).

The results of our laboratory studies were confirmed in field experiments where a smaller trap containing 46.9 g of Sofnocat 682 was used to purify air carrier gas cylinders on a RGA-3 analyser continuously monitoring ambient carbon monoxide levels. After eighteen months of “scrubbing” air carrier gas at a flow-rate of 20 ml/min, the trap still removed ≥99% of both carbon monoxide and hydrogen from an air cylinder containing 1.71 ppm (v/v) carbon monoxide and 2.80 ppm (v/v) of hydrogen. This field Sofnocat 682 trap was also tested with high-purity nitrogen [0.198 ppm (v/v) CO, 0.018 ppm (v/v) $H_2$] whereupon a carbon monoxide removal efficiency of cu. 91% was still present as compared to a >99% removal efficiency prior to the field trials. No hydrogen breakthrough was observed but the test input level of 0.018 ppm (v/v) hydrogen in nitrogen was approaching the detection limit of the analyser. No long term tests were performed in the field with nitrogen carrier gas, but since some degradation in performance was observed for nitrogen on the Sofnocat 682 trap that had been used for eighteen months with air, it is recommended that a larger trap changed at more frequent intervals be used if nitrogen carrier gas were to be used in the field. According to the manufacturers, "spent" Sofnocat 682 can be readily reactivated by heating in hydrogen diluted with dry nitrogen at cu. 50°C [34].

The results of the use of Sofnocat 682 as a simple scrubber for the provision of "zero grade" diluent gas in a simple one step dilution system for the provision of sub-ppm (v/v) calibration standards are shown in Fig. 2. A standard containing 1.82 ppm (v/v) of carbon monoxide can readily be diluted over two orders of magnitude down to *ca.* 0.020 ppm (v/v) with excellent linearity of detector response ($r^2$ = 0.999). The standard deviation from replicate dilutions is shown in Fig. 3, where it can be seen that the mean standard deviation for the dilution procedure is ca. 1.2%, of which ca. 0.5% is the observed reproducibility of the CO analyser itself. The greater standard deviations observed at 50 and 100-fold dilution are a consequence of the increased detector noise at those levels. Since atmospheric carbon monoxide mixing ratios in clean Northern hemispheric air are about 0.1 ppm (v/v) [7], this simple one-stage dilution system is ideal for the preparation, either in nitrogen or air, of field calibration standards at around ambient concentrations from low ppm (v/v) certified commercial standards. Since the Sofnocat 682 catalyst trap also quantitatively removes carbon monoxide (and hydrogen) at flow-rates of *ca.* 1000 ml/min, accurate dilutions over three orders of magnitude can be made thereby allowing higher-concentration certified standards to be used. Although, in principle our system using Sofnocat 682 is applicable to the preparation of sub-ppm (v/v) hydrogen standards, no attempt was

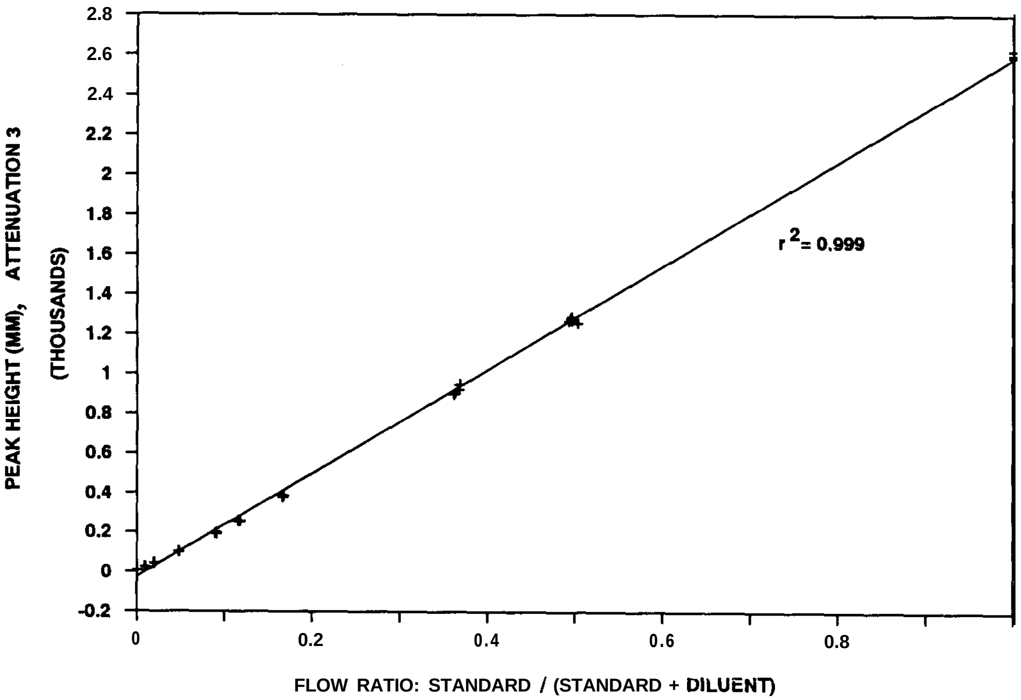

Fig. 2. Plot of the RCA-2 detector output versus dilution for the single stage dilution with "zero grade" air of a standard containing 1.82 ppm (v/v) carbon monoxide.

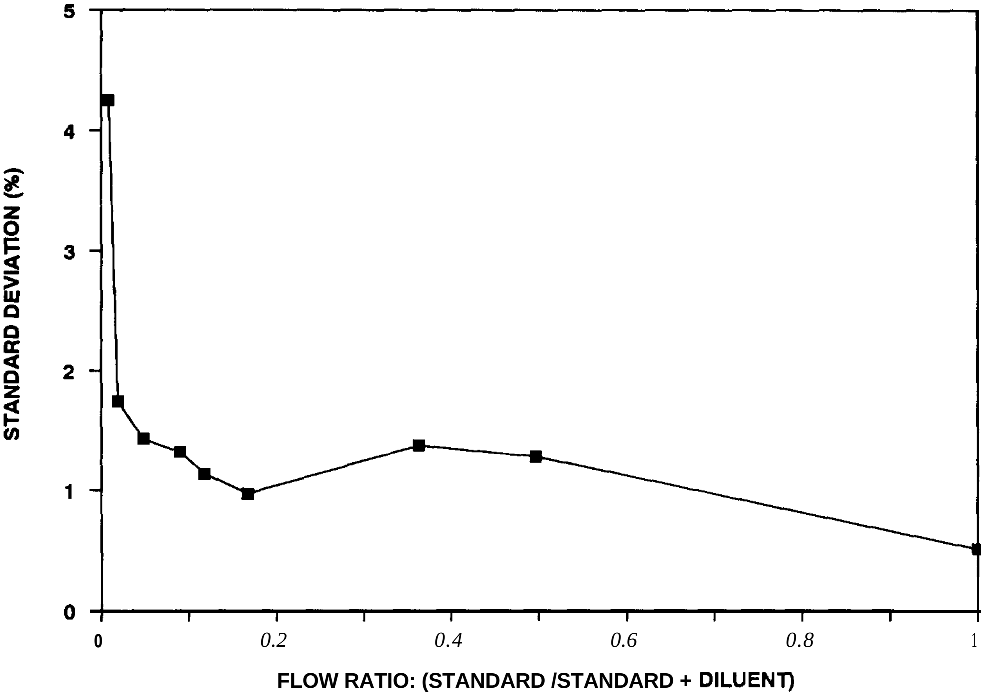

Fig. 3. Plot of the standard deviation (%) *versus* dilution for the single stage dilution with "zero grade" air of a standard containing 1.X2 ppm (v/v) carbon monoxide.

made to prepare such standards of hydrogen using this method since the mixing ratio of hydrogen in clean air is an order of magnitude higher than carbon monoxide, at which level quantification can readily be achieved using low-ppm (v/v) hydrogen standards. However the system could be used for the generation of sub-ppm (v/v) calibration levels of hydrogen for other applications.

Although our studies have been restricted to carrier gases employed on a mercuric oxide detector, we consider the use of Sofnocat as a gas purifier is applicable to other inert gases such as helium and argon and alternative detection techniques (*viz.* electron-capture [12], non-dispersive infrared [35,36], flame ionisation [37] and helium ionisation [17]) used for measuring low levels, particularly ambient mixing ratios, of carbon monoxide and/or hydrogen.

## ACKNOWLEDGEMENT

We are indebted to Mr. M. Law for performing the initial carbon monoxide and hydrogen analyses.

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