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Reference Materials for the Pyrolysis Gas-chromatographic Determination of Ammonia, Nitrogen, Nitrogen Monoxide, Carbon Monoxide, and Carbon Dioxide

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Synopsis. Four compounds are proposed as the reference materials to calibrate the pyrolysis gas chromatograph in the determination of inorganic gases: $[Co(NH_3)_5Cl]Cl_2$ for NH_3, $[Co(NH_3)_5NO_2]Cl_2$ for N_2, $[Co(NH_3)_5NO]Cl_2$ for NO, and PbC_2O_4 for both CO and CO_2. On pyrolyses, the gas evolution of these compounds were stoichiometric, and the peak area corresponded fairly well to the weight of the compound. Under the condition employed, 7.3—138 μmol of NH_3, 2.2—67 μmol of N_2, 2.0—61 μmol of NO, 0.84—26 μmol of CO, and 2.5—76 μmol of CO_2 were analyzed by using 0.5—15 mg of the compounds.

Pyrolysis gas chromatography (PGC) has been developed as a technique for the structural characterization of organic polymers.[1] In our previous papers,[2] the PGC technique was successfully employed for the quantitative determination of the gaseous products, N_2 and N_2O, evolved upon the pyrolyses of the series of Co(III)-ammine and Mo- or W-nitrosyl complexes. In practical use, however, it was not quite advantageous to calibrate the PGC instrument with standard gas, since, by the method using a gas syringe, hardly any standard gas was injected exactly into a furnace heated at a high temperature wherein a sample was pyrolyzed. Therefore, it seemed desirable to calibrate the instrument under conditions identical to those for the pyrolysis of sample. The PGC technique can be expected to be more useful if the PGC instrument can be easily calibrated with such reference compounds as evolve the desired gas stoichiometrically upon the pyrolysis.

In the present article, four inorganic compounds have been recommended as useful references for the calibration of the PGC instrument for the determination of NH_3, N_2, NO, CO, and CO_2.

Experimental

Materials. The compounds, $[Co(NH_3)_5Cl]Cl_2$,[3] $[Co(NH_3)_5NO_2]Cl_2$,[4] $[Co(NH_3)_5NO]Cl_2$,[5] and PbC_2O_4,[6] were prepared by the published manner and were purified by repeated recrystallizations.

Measurements. The PGC measurements were carried out by the use of a YANACO G 80 TCD gas-chromatographic instrument equipped with a YANACO GP 1018 pyrolysis pippeter, following the manual. An 0.5—15.0 mg aliquot of the compounds was transferred into a platinum crucible (16 mm³), and then the crucible was inserted into the pyrolysis pipetter, whose furnace had been kept at the desired temperature. The compound was pyrolyzed instantly in helium gas, and the gaseous products were subsequently swept by the helium-gas carrier into the GC separation column. The peak area was recorded on an integrator. The PGC conditions are tabulated in Table 1.

Results and Discussion

The four compounds considered here can be easily obtained and stored in a pure and stable form. The purities of the cobalt complexes were examined by means of cobalt, ammonia, and chloride analyses, and that of lead oxalate, by lead analysis. The thermal-decomposition processes of these compounds have already been established to follow Eqs. 1—4;[2,6,7] they have also been confirmed, as is shown in Table 2.

$$6[Co(NH_3)_5Cl]Cl_2 \longrightarrow 22NH_3 + N_2 + 6NH_4Cl + 6CoCl_2$$

$$6[Co(NH_3)_5NO_2]Cl_2 \longrightarrow 7N_2 + 22NH_3 + 12H_2O + 6CoCl_2$$

$$[Co(NH_3)_5NO]Cl_2 \longrightarrow NO + 5NH_3 + CoCl_2$$

$$2PbC_2O_4 \longrightarrow CO + 3CO_2 + Pb_2O$$

The relation between the amount of gas, μmol, calculated from Eqs. 1—4 and the peak-area counts, recorded on the integrator is shown in Fig. 1. The correlation curves in Fig. 1 indicate that the amount of gas detected corresponded linearly to the weight of the compound provided for the pyrolysis. In the pyrolysis temperature range given in Table 1, the cor-

Table 1. PGC conditions

Gas	Reference material	Temperature range for pyrolysis/°C	Column Packing	Column length/m	Column temp/°C	TCD temp/°C	Retention[e] time/s
NH_3	$[Co(NH_3)_5Cl]Cl_2$	320—500	Porapak N[a]	1.5[c]	160	170	58—67
N_2	$[Co(NH_3)_5NO_2]Cl_2$	410—500	Molecular[b] Sieve 5A	3.0[d]	60	110	22—27
NO	$[Co(NH_3)_5NO]Cl_2$	180—500	Molecular[b] Sieve 5A	1.5[c]	80	110	63—70
CO	PbC_2O_4	410—500	Silica gel[b]	3.0	80	110	38—41
CO_2	PbC_2O_4	410—500	Silica gel[b]	3.0	80	110	69—73

Column: stainless steel; 3 mm i.d. a) 50—80 mesh. b) 60—80 mesh. c) In order to reduce lingering tailing, a short column was preferred. d) In order to separate N_2 completely from adsorbed NH_3 a long column was preferred. e) The flow rate of the He-gas carrier was 25 cm³/min.

TABLE 2. ANALYTICAL CONFIRMATION OF DECOMPOSITION PRODUCTS

Reference material	$CoCl_2$		NH_4Cl	NH_3[d]	Pb[b]	CO_2[e]
	Co[b]	Cl[c]	Cl[c]			
$[Co(NH_3)_5Cl]Cl_2$	23.57 (23.52)	28.73 (28.35)	13.93 (14.18)	24.96 (24.89)		
$[Co(NH_3)_5NO_2]Cl_2$	22.18 (22.58)	26.24 (27.21)		23.73 (23.89)		
$[Co(NH_3)_5NO]Cl_2$	24.25 (24.05)	28.79 (28.99)		23.54 (24.71)		
PbC_2O_4					69.87 (70.19)	22.30 (22.36)

a) Calculated values are given in parentheses. b) Determined by EDTA titration. c) Determined by the Volhard method. d) Determined by trapping the gas into a standard 0.05 M H_2SO_4 solution and then titrating the excess acid with a standard 0.1 M NaOH solution. e) Determined by trapping the gas into a standard 0.1 M NaOH solution and then titrating the excess alkali with a standard 0.05 M H_2SO_4 solution (1M = 1 mol/dm^3).

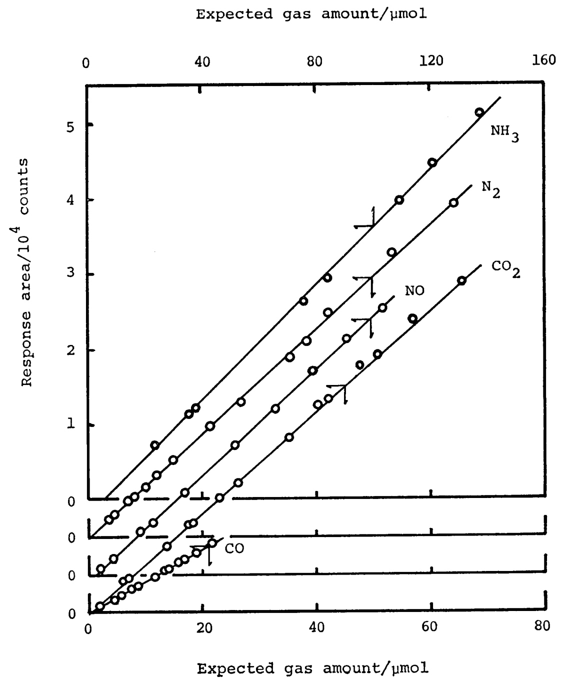

Fig. 1. Calibration curves.

TABLE 3. CALIBRATION CONSTANTS AND PRECISION; $F = aA - b$

Gas	*a*	*b*
NH_3	383 (±3)	2386 (±340)
N_2	701 (±6)	383 (±194)
NO	706 (±7)	1121 (±186)
CO	426 (±2)	160 (±30)
CO_2	676 (±5)	395 (±210)

F = Response area/counts. A = Expected gas amount/μmol.

relations fell on a straight line. Under the conditions employed, the weights of the compound provided for the pyrolysis were restricted within the range from 0.5 to 15 mg. Hence, the amount of gas detected corresponds to 7.3—138 μmol for ammonia, 2.2—67 μmol for nitrogen, 2.0—61 μmol for nitrogen monoxide, 0.84—26 μmol for carbon monoxide, and 2.5—76 μmol for carbon dioxide. In the correlation curves for NH_3, N_2, NO, CO, and CO_2 in Fig. 1, extraplotation gives a negative vertical intercept; this may be caused by the chromatographic tailing of these gases, which has often been observed in their GC peaks.[8] The calibration constants and precision are shown in Table 3.

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