It needs be added that the silicate catalyst had to be regenerated for removal of tar between runs in a stream of O_2 at 550°C.

Isolation of 2-^{13}C and 3-^{13}C *enriched pyrroles.* The major part of NH_3 was removed as described above. The 0°C remainder was distilled *in vacuo* into a tube, containing 10 g of BaO. After 1 h shaking the dehydrated product was again distilled *in vacuo* into a small tube. Here, vapor fractions were first removed at 0°C, later at room temperature (24°C), until the initially higher pressure had dropped to 7.5 mm Hg, the pressure of saturated pyrrole vapor. After a final distillation of the remanence, 34 and 25 mg enriched pyrrole, respectively, was collected, representing a 20 % yield with respect to furan. Infrared spectra of the vapors at room temperature (p = 7.5 mm) in a gas cell of length 10 cm showed that these vapors contained no impurity (furan, NH_3, H_2O etc.), detectable in the 400—4000 cm^{-1} interval scanned on a Perkin Elmer Spectrophotometer 125 instrument. The spectra were, indeed, almost identical with the spectrum of ordinary pyrrole, the isotope effect being small. At the subsequent microwave investigation of the same vapors their purity was confirmed, and it could be seen that their isotopic enrichment is close to 22 %. Therefore, *no migration of* ^{13}C during the contact of the reaction mixture with the 400°C hot catalyst had taken place.

Preparation of ^{15}N *enriched pyrrole.* Since the furan to pyrrole conversion demands a considerable excess of NH_3 it was found more profitable to prepare ^{15}N-enriched pyrrole by pyrolysis of the ammonium salt of mucic acid,[5] $(CHOH)_4(COOH)_2$. 4.2 g (20 mmole) of mucic acid was stirred with 4 ml of water to a paste in a 60 ml flask and afterwards cooled and evacuated. 19.4 mmole gaseous, ^{15}N enriched (33 %) NH_3 was condensed and reacted with the acid in the same flask, after which excess water was removed *in vacuo* at room temperature. 6 g glycerol was added. After 12—24 h of standing the flask was connected to a special condenser for small quantities and kept for 15—20 min at about 200°C. The heterogeneous distillate (pyrrole, H_2O, $(NH_4)_2CO_2$, tar, etc.) was afterwards distilled *in vacuo* at room temperature. The new distillate (about 1 ml) consisted of water and droplets of pyrrole. After two contacts with 2 g of CaO (stirring) water was removed, but CaO had liberated a small amount of NH_3, contaminating the pyrrole. NH_3 was removed and pyrrole isolated as described for the ^{13}C enriched samples. The yield of ^{15}N enriched pyrrole of satisfactory purity was 180 mg (270 mmole). This represents a 14 % yield with respect to the enriched NH_3, or about 4 times as much as obtainable by reacting 20 mmole of enriched NH_3 to 3.00 mmole of furan.

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A Method for the Introduction of Submicrogram Samples into a Gas Chromatograph

ROLF BLOMSTRAND and JOSEF GÜRTLER

Department of Clinical Chemistry at Serafimerlasarettet, Karolinska Institutet, Stockholm, Sweden

In connection with quantitative analysis of steroids [1] the necessity arose of having at hand a simple method for the introduction of a known amount of a test mixture into the gas chromatograph. A number of well established methods of introducing liquids or solids into a gas chromatograph have been reported.[2-4] Such methods usually require modification of the injection system or rather elaborate devices.

The present paper describes a simple procedure for introduction of minute quantitaties into a gas chromatograph. The substance can be introduced with or without solvent. The absence of solvent has distinct advantages in quantitative analysis of steroids, fatty acids and amines, isolated from biological material. The major advantage is that a very minute sample can

be transferred quantitatively on the column. This is mostly impossible to do with the aid of a syringe. Furthermore the injection time may play an important role in the performance of the column. This difficulty is overcome when no solvent is present.

The device consists of a small platinum spiral approximately 1.5—2 mm in diameter and about 3 mm in length. The spiral is hooked into a small stand of pyrex glass as shown in Fig. 1. To apply a sample a solution is applied to the spiral a few microliters at a time and the solvent is allowed to evaporate. If one wants to increase the capacity of the spiral it is filled with a small piece of glass wool. When the desired amount of material has been applied to the spiral, the spiral is transferred to the top of a glass column. A straight glass column and Pye apparatus equipped with an ionisation chamber has been used.

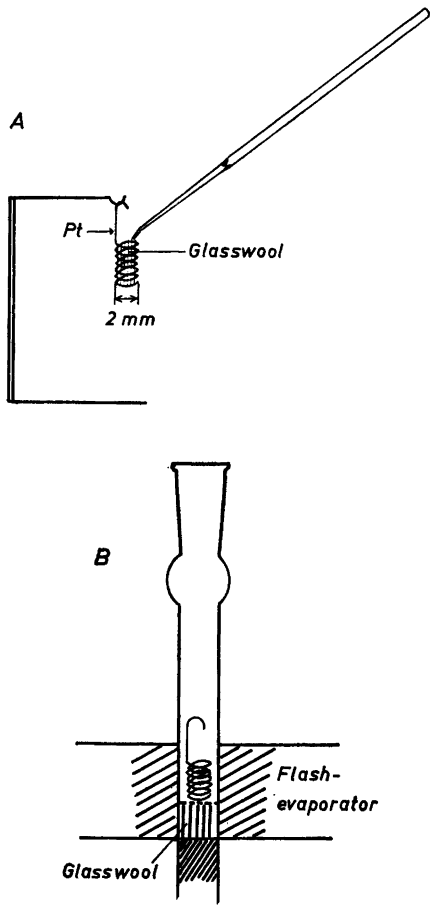

Fig. 1. A: Application of sample on a platinum spiral filled with glass wool.
B: Introduction of the sample on the column with the aid of the platinum spiral.

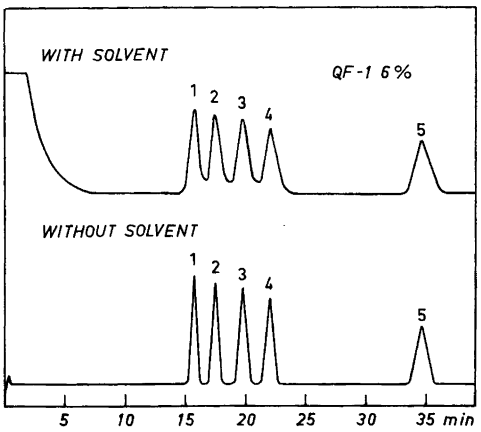

Fig. 2. Gas chromatograms showing difference between introduction of steroid mixture with and without solvent. Test mixture containing, 1. Androsterone, 2. Etiocholanolone, 3. Dehydroepiandrosterone, 4. Isoandrosterone, 5. 11-Keto-etiocholanolone. The test mixture was dissolved in hexane and chromatographed as methylsilylethers. Stationary phase: QF. 1 6 % by weight of solid support. Temperatures: Injection 250°C. Column and detector 207°C.

In Fig. 2 chromatograms are shown indicating the difference between injecting a steroid mixture with and without solvent. After two years our experience is that with most compounds the column performance will be better if the samples are introduced as solids.

Finally this method can be used for absolute calibration of a gas chromatograph. In Fig. 3 the platinum spiral has been loaded with increasing amounts of pregnandiol and the amount applied has been checked with a Cahn microbalance. Under the chosen conditions the ionisation chamber gives a linear response.

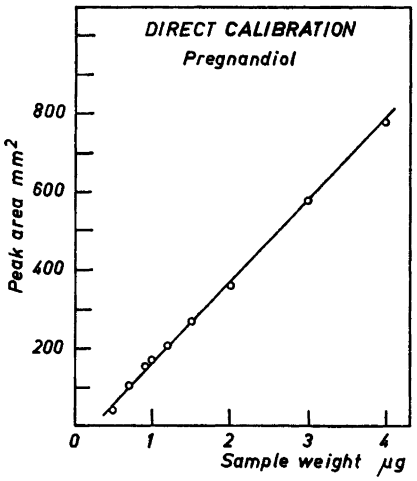

Fig. 3. Introduction of known amounts of pregnandiol without solvent showing linear response of the ionisation chamber. Stationary phase: Se-30 3 % by weight of solid support. Temperatures: Injection 245°C. Column and detector 210°C.

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On the Hydrolysis of Niobates in 3 M K(Cl) Medium

GEORG NEUMANN

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

The amount of information concerning ionic species in aqueous solutions of alkali metal niobates is rather limited. Using several different methods of investigation Jander and Ertel[1] concluded that the main species were $Nb_6O_{19}^{8-}$, $HNb_6O_{19}^{7-}$, and $(Nb_6O_{18}^{6-})_n$, where $n = 3$ or 4. However, later Lehné and Goetz [2] and more recently Leicht, Lehné and Rohmer [3] have studied niobate solutions by cryoscopy and emf measurements. They interpreted their data by assuming the species $Nb_5O_{16}^{7-}$, $HNb_5O_{16}^{6-}$ and $H_2Nb_5O_{16}^{5-}$ in the pH range 11 – 13.5, and they reported mononuclear or dinuclear species in still more alkaline solutions. Furthermore an X-ray study by Lindqvist [4] indicated that hexanuclear niobate groups were present in the solid isopolyniobate, "7 Na_2O·6 Nb_2O_5·32 H_2O".

The primary object of the present work was to decide whether hexa- or pentaniobates predominate in solution. During the experiments many difficulties were encountered but some preliminary work is reported here.

A series of emf-titrations were carried out in which the total niobium concentration, B, was kept constant whereas the total OH^--concentration in excess over $Nb(OH)_5$, $-H$, was varied. The variation of the activity factors was minimized by adding KCl to the solutions and keeping $[K^+] = 3$ M. $[OH^-]$ was obtained from the emf of the cell

$$-\text{Pt, } H_2\,(1\text{ atm})/\text{niobate solution S}/\text{SE} +$$

where SE is the reference electrode. SE = 3 M KCl/3 M KCl (saturated with AgCl)/Ag, AgCl. The emf may be written $E = E_0 - 59.15 \log [OH^-] + j[OH^-]$. By separate experiments without niobate in S the constants E_0 and j were determined; the latter was remarkably low (1 mV/M). From B, $-H$ and $[OH^-]$ the average negative charge per Nb atom was obtained as $Z = (-H - [OH^-])/B$.

Experimental. Two different potassium niobates were used for the preparation of the stock solutions.