Detection and Characterization of Acetylenes by Hydration to Carbonyl Compounds and Formation of 2,4-Dinitrophenylhydrazones

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A method has been developed for differentiating the acetylene from the olefin functional group, both of which decolorize both bromine and permanganate, by hydrating with a boron trifluoride, mercuric oxide, and trichloroacetic acid catalyst mixture. The carbonyl compounds formed are treated with 2,4-dinitrophenylhydrazine and a phenylhydrazone is formed by addition of methanolic potassium hydroxide to produce a wine red color. Other functional groups were tested to determine the applicability of this reaction to the qualitative organic analysis scheme. This reaction was also used to characterize terminal and symmetrically substituted acetylenes by the melting points of the dinitrophenylhydrazones and semicarbazones prepared from the carbonyl compounds. The qualitative test also permits the detection of the acetylene in the presence of an olefin bond in either the same molecule or in mixtures.

PRESENT QUALITATIVE tests for the acetylene bond employ the bromine (20) and permanganate (5) reductions which give the same signs of reaction with olefins. For terminal acetylenes, reagents which produce solid products are alcoholic silver nitrate, ammoniacal cuprous chloride (3), and phenyl isocyanate with the acetylene Grignard compounds RC=C-MgX (9). These and other reagents for characterizing acetylenes such as 2,4dinitrosulfenyl chloride (10), and thioacetic acid under free radical conditions (2), have the drawbacks that the derivatives are either difficult to purify, are explosive, require too much time for preparation, or give only one functional derivative.

The epoxidation-hydroxamation (17) test for olefins distinguishes them from acetylenes which do not react under these conditions. While this test is suitable for differentiating between



With BF₃ as catalyst in CH₃OH, A is (CH₃O.BF₃) - and HA is CH₃O-BF₃

olefin and acetylene functional groups, it is, nevertheless, not suitable for positive identification of the triple bond. Hydration of the acetylene to a carbonyl function, which is detected with the dinitrophenylhydrazine reagent, complements the olefin test and also provides positive identification for the acetylenic functional group:



ALKYNE HYDRATION

Hydration of acetylenes with a sulfuric acid-mercuric sulfate catalyst (θ) is accompanied by rearrangement and polymerization that are produced by the mineral acid and high temperature encountered in the reaction.

Nieuwland, Vogt, and Foohey (11) synthesized ketals from acetylenes with a catalyst mixture of mercuric oxide and methoxyfluoboric acid which is prepared by the reaction between methanol and boron trifluoride:

$$\begin{array}{c} \mathrm{CH}_{3}\mathrm{OH} + 2 \mathrm{BF}_{3} \rightarrow \\ \mathrm{H}\\ & \downarrow \\ 2 \mathrm{CH}_{3}\mathrm{O} \rightarrow \mathrm{BF}_{3} \xrightarrow{+ \mathrm{HgO}} \mathrm{H}_{2}\mathrm{O} + \\ [\mathrm{Hg}(\mathrm{CH}_{3}\mathrm{OBF}_{3})_{2}] \rightarrow 2 \mathrm{CH}_{3}\mathrm{OBF}_{2} + \mathrm{HgF}_{2} \end{array}$$

The reactions in alkyne hydration under these conditions have been summarized by Hennion, Vogt, and Nieuwland (8) and are shown in the modified flow sheet above.

The ethylidene derivatives are readily hydrolyzed to ketones with dilute aqueous potassium carbonate. The boron trifluoride catalyst affords a rapid and relatively simple method for transforming alkynes to carbonyl compounds inasmuch as it is effective at low concentrations and results in a minimum of polymerization.

Hydration of alkynes was applied by Wagner (21) to the quantitative estimation of acetylene bonds by using standard base to titrate the hydrochloric acid liberated when the ketone is oximated with hydroxylamine hydrochloride. A boron trifluoride mercuric oxide catalyst was used for the analysis of the low

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molecular weight acetylenes 1-pentyne, 2 - butyne, and 3 - methyl - 1 - butyne. Siggia (19) carried out similar quantitative determinations with several acetylenes but employed a mercuric sulfatesulfuric acid mixture as a catalyst.

CRITERIA FOR IDEAL QUALITATIVE FUNCTIONAL GROUP TEST

Acetylene hydration followed by dinitrophenylhydrazone formation meets the requirements of an ideal functional group test (17) in that the sign of reaction is based on a chemical change in the substrate and the reactions occur with acetylenes which differ greatly in reactivity. These reactions also detect low concentrations of substrate, and produce solid derivatives suitable for characterization.

REAGENTS AND SOLUTIONS

Alkynes. The acetylenes used for characterization, obtained from Farchan Research Laboratories (Wickliffe, Ohio), were represented to be free from olefin impurities because of their synthesis from acetylides and alkyl halides. The epoxidation-hydroxamation test (17) was used to establish the absence of olefin impurities and the purity of the acetylenes was checked by determining the refractive index with a Bausch & Lomb Abbé refractometer at 25° C. and comparing these results with the literature values (see Table V).

Boron Trifluoride Catalyst. For each test, the catalyst suspension is prepared by addding to a 3-inch test tube 100 mg. of red mercuric oxide, approximately 10 mg. of trichloroacetic acid, 0.25 ml. of methanol, and 0.15 ml. of boron trifluoride etherate. The catalyst is warmed in the water bath at 50° to 60° C. for 1 minute prior to use in the hydration reaction.

Boron Trifluoride Ethyl Ether (purified). Eastman Organic Chemicals No. 4272.

Mercuric Oxide. Baker & Adamson No. 1969, ACS reagent grade.

Potassium Carbonate. Baker & Adamson No. 2102. A 10% solution was prepared by dissolving 10 grams in sufficient water to make the final volume 100 ml.

2,4-Dinitrophenylhydrazine Reagent. Suspend 10 grams of 2,4-dinitrophenylhydrazine (Eastman No. 330) in 850 ml. of methanol, add 170 ml. of 36% hydrochloric acid, and store the solution in a brown bottle with a rubber stopper.

Semicarbazide Reagent. A solution is prepared of 1.11 grams of semicarbazide hydrochloride (Eastman No. 226) in 5 ml. of water. Pyridine is added to catalyze the reaction with the ketones.

EXPERIMENTAL PROCEDURES

Epoxidation - Hydroxamation Test for Alkenes. The procedure and reagents used are described in a preceding paper by Sharefkin and Shwerz (17), Qualitative Detection of Alkynes. Into a 3-inch test tube are placed approximately 60 mg. of acetylene and 2 ml. of methanol. The warmed catalyst suspension, prepared as described above, is added to the solution of the acetylene. One half hour later, 3 ml. of a 10% potassium carbonate solution are added and the mixture centrifuged. The mixture is tested by adding the dinitrophenylhydrazine reagent until the solution is acid. If a ketone is present, a yellow to orange precipitate is formed. The presence of a dinitrophenylhydrazone is confirmed by taking a small portion of the liquid and making it alkaline with 2M methanolic potassium hydroxide to produce a blood red color.

Characterization of Alkynes. Using an 8-inch test tube, 1 gram of acetylene is dissolved in 3 ml. of methanol.

The warmed catalyst suspension from the 3-inch test tube is added to the solution of the acetylenic compound, the small test tube rinsed with 1 ml. of methanol, and the rinse solution added to the large test tube. With most acetylenes, an exothermic reaction begins a few minutes after the warm catalyst suspension is added. Where this does not occur, reaction is initiated by warming for a few minutes in a water bath at 50 to 60° C. As the reaction progresses, the color of the red mercuric oxide changes to a dark gray and the color of the supernatant liquid after reaction ranges from colorless to yellow. After approximately 30 minutes, 2 to 3 ml. of a 10% aqueous po-tassium carbonate solution are added to hydrolyze the ketal. A grayish black precipitate may form and in some cases there is a visible separation of two layers. The mixture is filtered into a test tube and the residue washed with 2 to 3 ml. of methanol.

The combined filtrates containing the carbonyl compound are used to prepare the dinitrophenylhydrazone and the semicarbazone by adding 2 to 3 ml. of either reagent to the filtrate, and with the semicarbazone this is followed by 0.5 ml. of pyridine. The solutions are then warmed on a water bath at 50° to 60° C. for approximately 15 minutes. The formation of a hydrazone is confirmed as described above for the qualitative detection of acetylenes. If a precipitate is not obtained, the solution is chilled to 10° C. to induce crystallization and with some compounds the derivatives are obtained only after the solution has been kept for 1 or 2 days at 10° C. The crude derivatives are recrystallized from mixtures of methanol or ethanol and water. Melting points of the solid derivatives are determined with Anschutz thermometers and are uncorrected. The percentage yields of the carbonyl compounds are calculated from the weight of the purified derivative.

Differentiation of Olefin from Other Functional Groups. A number of compounds having other representative functional groups were treated using the boron trifluoride catalyst under the same conditions employed for detecting acetylenes and the product(s) were similarly hydrolyzed and tested with the dinitrophenylhydrazine reagent and then with methanolic potassium hydroxide. In each case, a control test was carried out by treating the compounds with the dinitrophenylhydrazine reagent before the hydration.

Lower Limits of Alkyne Detection. The terminal alkyne, 1-pentyne, was used to establish the sensitivity of this reaction for the detection of small quantities of acetylenes. Solutions of this alkyne were diluted and tested to determine the smallest amount

Table I. Qualitative Detection of Alkynes by Hydration and Dinitrophenylhydrazone Formation

| Compound | Be- fore Hy- dra- tion | After Hy- dra- | Epoxida- tion Test |
|------------------------|------------------------------------|----------------------|--------------------------|
| | CION | 01011 | 1050 |
| 1-Pentyne | - | + | - |
| 1-пехупе | _ | + | - |
| 2-Hexyne | | + | - |
| 3-flexyne | | + | |
| 1-neptyne | | + | - |
| 1-Octyne | | + | |
| 2-Octyne | | + | |
| 4-Octyne | | + | |
| 2 Nonuno | _ | + | - |
| 2-Nonyne 2 Nonyno | - | + | |
| A Nomero | | + | - |
| 4-Nonyne | - | + | |
| 2 Decyne | | | - |
| 2-Decyne | - | + | - |
| 3-Decyne | - | + | |
| 4 Decyne | - | + | |
| 5-Decyne | | + | - |
| 1-Undecyne | - | + | — |
| 1-Dodecyne | _ | + | — |
| Dipnenyi- | | | |
| acetylene | | + | - |
| Phenylacetylene | _ | + | - |
| Metnyipnenyi- | | | |
| acetylene | | + | - |
| 5-Metnyl-1- | | | |
| nexyne | | + | - |
| Metnyl p-nitro- | | | |
| pnenylpropio- | | | 37 |
| late | _ | | Not tested |
| Metnyi m-nitro- | | | |
| pnenyipropio- | | | N. J. Jackson |
| late | | | Not tested |
| Metnyl p-chloro- | | | |
| pnenyipropio- | | | NT 1 1 . 1 . 3 |
| Matherly montherly | - | -+- | Not tested |
| Metnyl p-metnyl | | | |
| pnenyipropio- | | | NT |
| late | _ | + | Not tested |
| p-Chlorophenyl- | | | Nutraina |
| Propione acia | _ | + | Not tested |
| rnenyipropione | | 1 | No. 4 Acres 3 |
| | - | + | Not tested |
| Acetylene di- | | | |
| carboxyne | | | NT |
| Dimenthal | | + | Not tested |
| Dimetnyi- | | | |
| dicorbourdie | | | |
| ulcarboxyne | | | Net tested |
| Aciu Mathulhutuu al | | + | Not tested |
| Methylputynol | + | + | Not tested |
| Fthurnylouolo | | + | TNOT TESTED |
| howaral | , | , | Not tosts |
| Diphonulhour | + | + | Not tested |
| Dimethylhour -1 | | + | Not tested |
| Phonylbytymol | | + | Not tested |
| T Den A DOR PARTON | | + | TAOP rested |

| hydrazone Formatio Functional | n Test Groups | on Various s |
|----------------------------------|--|-----------------|
| | Qualitative Dinitrophenyl- hydrazone Test | |
| | Before BF ₈ | After BF3 |
| Compounds | treat- ment | ment |
| Alcohols | | |
| 2-Phenylcyclohexanol | _ | - |
| Triphenylcarbinol | - | - |
| Methallyl alcohol | + | Not tested |
| Phenols | | |
| p-Nitrophenol | | |
| Methyl p-hydroxy- | | |
| benzoate | - | - |
| Esters | | |
| Methyl p-nitro- | | |
| benzoate | | |
| Dyanoetnyl acetate | | - |
| Olefing | - | - |
| 11 Triagona | | |
| Indene | | |
| 1 1-Diphenylethylene | _ | _ |
| Vinvlevelohexane | | _ |
| 1-Pentene | | - |
| Cyclopentene | + | Not tested |
| β-Pinene | <u> </u> | _ |
| Methylcyclohexene | + | Not tested |
| Ethers | | |
| Butadiene monoxide | + | Not tested |
| Benzyl ether | ÷ | Not tested |
| Ethyl ether | _ | |
| Tertiary amines | | |
| Pyridine | | |
| Halogen compounds | | |
| Chloroform | _ | |
| Oxylbromide | | _ |
| · | | |

II. Hydration-Dinitrophenyl-

Table

that would undergo hydration and produce sufficient ketone for the formation, isolation, and purification of a solid dinitrophenylhydrazone whose melting point could be used to characterize the original alkyne. When this concentration was determined, the solution was diluted until no positive qualitative test for ketone formation was obtained by addition of the dinitrophenylhydrazone to 2M methanolic potassium hydroxide.

Differentiation of Olefins (Alkenes) from Alkynes. The epoxidation-hydroxamation test for olefins of Sharefkin and Shwerz (17), was applied to all the alkynes tested to both check and complement the data obtained from the boron trifluoride catalyzed hydration reaction.

DISCUSSION OF RESULTS

Detection of Alkynes. The consistency of the results in Table I for the boron trifluoride catalyzed hydration of a large number of acetylenic compounds and the detection of the carbonyl compounds formed with the dinitrophenylhydrazine reagent for carbonyl compounds indicate that there is a wide spectrum of acetylene reactivity in the hydration reaction and that these reactions comprise a general test for the acetylene functional group. The epoxidation-hydroxamation olefin test was carried out simultaneously with each acetylene sample to rule out the presence of olefins as contaminants and acetylation followed by hydroxamation was applied to all samples tested to exclude the presence of alcohols or other functional groups that would interfere with the hydroxamation tests. phenylhydrazine reagent. No reaction was observed with methylpentynol, diphenylhexyndiol, dimethylhexyndiol, and phenylbutynol. The positive tests with methylbutynol and ethynylcyclohexanol are attributed to the acid in the dinitrophenylhydrazine reagent which initiates the Rupe Rearrangement (1, 7, 14) of hydroxyacetylenes to alpha-, beta-unsaturated carbonyl compounds (15).



The positive test for a ketone obtained after hydration of the acetylene dicarboxylic acid in this reaction also points up the wide latitude of this reagent inasmuch as electron attracting carboxyl groups usually decrease the ability of olefin bonds to react with electrophilic reagents such as bromine, permanganate, and peracetic acid. The two compounds giving negative tests, methyl *p*-nitrophenylpropiolate and methyl *m*nitrophenylpropiolate, did not respond even though the concentration of the catalyst was increased five-fold.

The permanganate, bromine, Friedel-Crafts acylation to ketones, and epoxidation-hydroxamation tests depend on the nucleophilic character of the alkene substrate. Acetylenes differ from olefins in that they react less readily with electrophilic reagents because of their cylindrical molecular orbitals, smaller carbon to carbon distance, and greater overlap of pi orbitals which result in a firmer binding of their pi electrons. Conversely, they are more susceptible to attack by nucleophiles and it may be presumed that the strongly electrophilic boron trifluoride catalyst produces an electrophilic carbonium ion which reacts with the nucleophilic water molecule.

In testing for acetylenes by this procedure, false positive tests from carbonyl compounds present as impurities or produced by the strong acid in the dinitrophenylhydrazine reagent were avoided by treating all the alkynes tested with this reagent before hydration and then applying the hydration reaction only if the test was negative. The results obtained with the acetylenes tested are listed in the first two columns of Table I and are uniformly good except for the positive reactions obtained with two of the six α -hydroxyacetylenes that were treated with the dinitro-

Specificity for Other Functional Groups. To determine the general applicability of the acetylene hydration reaction in qualitative organic analysis, this test was applied to compounds containing various functional groups. The hydration reaction with the boron trifluoride catalyst was applied only when the substrates first were found not to react with the dinitrophenylhydrazine reagent. The results of these tests summarized in Table II for alcohols, phenols, esters, alkenes, ethers, and tertiary amines, are generally negative for the initial test with the dinitrophenylhydrazine reagent and are negative after the hydration reaction. The false positive tests prior to hydration are attributed to samples having carbonyl compounds as impurities and are expected with both the olefin oxides and alkenes that have undergone air oxidation to epoxides. In these cases, the hydrochloric acid in the dinitrophenylhydrazine reagent causes a pinacol-pinacolone rearrangement to carbonyl compounds.

The negative tests with the dinitrophenylhydrazine reagent that are obtained with olefins both before and after treatment with the boron trifluoride catalyst may be used to differentiate them from the alkynes. In the solubility classification of the scheme for qualitative organic analysis, both types of unsaturated hydrocarbons are in the same group of hydrocarbon neutrals, N_h or N, that are soluble in cold concentrated acid but the bromine and permanganate tests for unsaturation do not discriminate between these two homologous series. The negative hydration reaction with olefins and positive test with acetylenes provide a technique for differentiating between these two functional groups when used to complement the Friedel-Crafts acetylation (18) and epoxidation-hydroxamation (17) tests for alkenes developed in previous papers according to the scheme indicated in Table III.

Characterization of Alkynes. The acetylenes listed in Table IV were hydrated with the boron trifluoride catalyst mixture and the carbonyl compounds formed were converted to their dinitrophenylhydrazones and semicarbazones to determine whether the points melting of \mathbf{these} solid derivatives could be used to identify the alkynes. The observed melting points of the dinitrophenylhydrazones

| Table | III. Qualitative Tests for | Distinguishing Ole Tests | efins and Acetylenes | | |
|--|---|---|--|--|--|
| Functional group | Friedel-Crafts acetylation and reaction with dini- trophenylhydrazine | Epoxidation- hydroxamation | BF ₃ Catalyzed hydration and reaction with dinitro- phenylhydrazine | | |
| Olefin Acetylene | + | + - | - + | | |
| Table IV. Relative Epoxidation Rates of Olefins and Acetylenes | | | | | |
| H—C≡C—I R—C≡C—I R—C≡C—I | H Immeasurably slow H 0.1 R 0.5 | $\begin{array}{l} H_2C = CH_2 \\ RCH = CH_2 \\ R_2C = CH_2, RCH \\ R_2C = CR_2 \end{array}$ | 1.0 20.0 =CHR 500 Immeasurably fast | | |

Product(s) M.P. of DNPH^b Derivative M.P. of S.C.^c Derivative of Yíeld₄ Acetylene R.I.ª Hydration Obs. Lit. Obs. Lit. 1-Pentyne 1.3888 2-Pentanone 144 - 14514526; -1.3890 1.3989 107-107.5 106 1-Hexyne 2-Hexanone 118-119.5 1213;17 1271.402125.6-127.6 124-127 2-Hexyne 1.4136 2-Hexanone 106 1.4143-Hexanone 130116-117 4; 6149-151 1123-Hexyne 3-Hexanone 110-111 1.4115-;9 -----1.4115 73-73.5 89, 73-74 1231.4092122.8-123.8 1-Heptyne 2-Heptanone 5;13 123-124 1.4086 741.4140 124-125 64-65 1-Octyne 2-Octanone 58118-118.5 15;9 1.417258 117-117.5 1231.42852-Octyne 2-Octanone 117-117.5 1.4353-Octanone 64 - 65117-117.5 92-93 96.4-97.2 4-Octyne 1.42214-Octanone 41 - 4341 1.42480.4;22-Nonanone 56.555 - 56118-120 118-119 1-Nonyne 1.42115;25 $\begin{array}{c}1.423\\1.431\end{array}$ 57.555-56/ 118.7-118.8 118 2-Nonyne 2-Nonanone -; 16119 1.4343-Nonanone 111-112 1.42933-Nonvne 3-Nonanone 46.5 96-98 7;16 1.429547.5 73–74 85; 67, 145 4-Nonanone 57 - 584-Nonyne 1.42864-Nonanone 68-70 -;6 70 5-Nonanone 90, 89-90 124, 1-Decyne 1.4262-Decanone 122 - 123-; 17 1261.442-Decyne 2-Decanone 119.4-120 -;6 3-Decanone 100-101 3-Decyne 1.43413-Decanone _ 1.43694-Decanone 51 - 52122-123 7;10 4-Decvne 1.4344-Decanone 91.5 - 93 $\begin{array}{c}1.436\\1.433\end{array}$ 5-Decanone 5-Decyne 60-61.5 57.5 - 589 6;10 5-Decanone 1.4313 1-Undecyne 1.4342 2-Undecanone 61 - 6263 121 - 122.5122 - 1237;15 122-122.5 1.42851-Dodecyne 1.43477.4-77.9 2-Dodecanone 81 120.5-121.5 122 - 12310;6 1.4318 5-Methyl-1-1.4059 5-Methyl-2-91.5-92 95140.6-141 142 - 1436;4 hexyne 1.4050 hexanone 238-240 237, Phenyl-238.4-240.2 Acetophenone 195 - 196198-199 7;34 ___ acetylene 249-250 16; 20 Deoxybenzoin 202-203.5 204 146 Diphenvlsolid 148 acetylene 147 Methylphenyl-1.5634Propiophenone 191 acetylene 1.563Phenylacetone 156

^a First value is observed at 25° C.; second is literature value. ^b Dinitrophenylhydrazone. ^c Semicarbazone. ^d Yields are of dinitrophenylhydrazone and semicarbazone derivatives, respectively. ^e Percentage nitrogen: Calcd. 22.70; obsd. 22.90%. ^f Melting point of derivative prepared from 2-nonanone. ^e Percentage nitrogen: Calcd. 19.72; obsvd. 19.40%

Table V. Dinitrophenylhydrazone and Semicarbazone Derivatives of Ketones Prepared by Acetylene Hydration

obtained, as well as the literature values. are given in Table V.

Terminal and symmetrically substituted acetylenes yield only one hydration product, the methyl or symmetrical ketone, respectively. Hydration of unsymmetrical acetylenes differs in that it results in a mixture of two ketones. The data in Table V show that the procedure gives inconclusive results with these acetylenes because of the difficulty in separating the mixture of products formed.

The epoxidation-hydroxamation test was used with all the acetvlenic compounds in Table I and found to give negative results which are listed in column three. These observations are not unexpected in view of the weaker nucleophilic character of the acetylene than the olefin bond and the lesser availability of the pi electrons of the triple bond is reflected in their relative reaction rates of epoxidation of the acetylenes listed in Table IV (13).

Epoxidation of acetylenes to produce oxirenes initially is not only slower but was also found by Schlubach and Franzen (16) to result in cleavage of the triple bond to acids of shorter chain length. Because of this difference in reactivity, peroxyacetic acid may be employed for selective epoxidation of an olefin bond that is conjugated with a triple bond.

$$H H$$

$$Ar - C \equiv C - C = C - R + AcOOH \rightarrow$$

$$H H$$

$$AcOH + Ar - C \equiv C - C - R$$

The only terminal acetylene that did not form the expected ketone was 1octyne which was transformed by the catalyst to a ketone whose dinitrophenvlhydrazone and semicarbazone melting points corresponded to those listed for 3-octanone rather than 2-octanone. This may arise from the presence of a small amount of more reactive 2-octyne as impurity coupled with the low yield of derivative which is attributed to the short reaction time in hydration. Another possible route to formation of 3octanone is oxidation of the 1-octyne to an allvlic hydroperoxide which rearranges to a mixture of 2- and 3octanone in the presence of the electrophilic catalyst.

The large differences in the literature values for the melting points of dinitrophenylhydrazones and semicarbazones can be attributed to geometric isomerism and to a dynamic isomerization between different crystalline forms (4, 12).

Lower Limits of Detection. With 1-pentyne as substrate, the sensitivity of the boron trifluoride catalyzed hydration and formation of dinitrophenylhydrazone was 6 mg. for qualitative detection and 60 mg. for characterization of the acetylene by the melting point of the dinitrophenylhydrazone after purification by recrystallization. Care should be exercised in observing the color obtained from the dinitrophenylhydrazone and 2M methanolic potassium hydroxide inasmuch as the reagent may produce a brown-red color on standing.

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SCIENTIFIC COMMUNICATION

Specific Microdiffusion Method for the Determination of Fluorine Based on the Lanthanum-Alizarin Complexone Color System

SIR: As far as can be ascertained, the determination of fluorine by microdiffusion never before has been accomplished. The reason for this, undoubtedly, can be attributed to the lack of fluoride-resistant Conway dishes. The problem was solved, when modified plastic Conway dishes became available in 1959 (4). In these dishes fluorine is liberated as HF at room temperature with H₂SO₄, diffuses, and

is trapped in the center compartment with dilute NaOH.

It has been shown by Belcher, Leonard, and West (2) that the cerium (III) chelate of alizarin complexone (1,2 - dihydroxyanthraquinonyl - 3 methylamine-N:N-diacetic acid) produces a colored complex with fluoride ion. In an acetate buffer the red color of the cerium(III)-alizarin complexone changes to the lilac-blue of the double

complex. The test is carried out in an acetate buffer at pH 4.3. The same authors have described a quantitative procedure for the determination of fluorine in fluorinated organic compounds (1).

Chelating reactions of complexone with metal cations have been investigated by Leonard and West (3). It was found that in addition to the cerium(III) chelate of alizarin com-