The most obvious conclusion to be drawn from the data in Table I is simply that spin–spin coupling can exist between copper(II) ions in the structural class under discussion. It may also be important to point out that the magnitudes of the single–triplet splitting span a relatively wide range of energy, an observation which suggests that the strength of the interaction between the two copper ions may not be reflected directly by the energy-splitting alone. In speculation on this point, it may be offered that the various effects which contribute to the mechanism of the spin-coupling interaction may have different signs thus modulating the magnitude of the singlet–triplet splitting according to the relative importance of the contributing effects.

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A Modified Unterzaucher Procedure for the Determination of Total Oxygen in Organometallic Compounds

Sir:

The determination of oxygen in new research compounds has often been a missing link in the total elemental analysis of these compounds. In many instances, especially in the case of organometallic compounds, oxygen has either been determined by difference or been ignored. On the other hand, if a convenient and reliable method for the determination of oxygen were available, such an analysis would be extremely useful in helping ascertain the composition of such new compounds.

Previous methods for the determination of oxygen based on the Unterzaucher method have given perplexing, erratic results, due in part to the nonselectivity in absorbing the carbon dioxide produced.[1–4] This results in a lowering of both the sensitivity and the accuracy of the method. Several modifications of the Unterzaucher procedure have appeared.[5–7] However, none of these has dealt with the determination of oxygen in organometallic compounds.

In the past few years, several papers have appeared using the technique of neutron activation in the analysis of oxygen.[8,9] While this method does offer the possibility of determining the oxygen content of various chemical compounds including metal oxides, the overall costs and time required are such that neutron activation methods are not applicable to routine analyses.

Recently we reported our own modification of the Unterzaucher method for the determination of oxygen.[10] While this particular modification was developed for the determination of oxygen (5 ppm to several per cent) in organic compounds, we suggested the potential utility of the method to nonorganic, oxygen-containing compounds. The purpose of the present correspondence is to disclose to the practicing chemist the availability of a simple yet practical and precise method for the routine determination of oxygen in most organometallic and inorganic compounds.

The basic procedure, which has been previously described in detail,[10] involves the pyrolysis of a preweighed sample at 1050° in the presence of high purity carbon. This converts all the oxygen in the sample to carbon monoxide. The process is carried out in a stream of helium which is used to elute the pyrolysis products. These are then separated into carbon monoxide and other gases by means of a molecular sieve column in a gas chromatograph. The amount of carbon monoxide formed is determined using a thermal conductivity detector. Our procedure is applicable to the determination of oxygen not only in solids, but also liquid and gaseous compounds as well. No apparatus blank is required to obtain a useful measure of oxygen down to 10 ppm. Our method has the further advantage that very small sample sizes are required for the determination of oxygen in most compounds. In Table I, some representative sample sizes for compounds containing various percentages of oxygen are given.

TABLE I
CONVENIENT SAMPLE SIZES FOR THE DETERMINATION OF OXYGEN

% oxygen present	Sample size, mg
20–100	<0.5[a]
10–20	0.5–1.0
5–10	1.0–2.0
1–5	2.0–5.0
0–1 (trace)	5.0–30

[a] The sensitivity of the method is such that even smaller sizes are usable; however, weighing inaccuracies necessitate 0.5-mg samples.

Table II lists some typical oxygen-containing organometallic compounds which have recently been analyzed by our method, together with the calculated percentages of oxygen in each compound. These compounds contain a variety of metals, metalloids, phosphorus, halogens, etc., and are reasonably representative of the new types of organometallic compounds which are being synthesized daily in laboratories around the world.

We should point out that special consideration must be given compounds being analyzed for oxygen in the presence of fluorine by our method. A preconditioning of the pyrolysis tube is required in this instance to prevent the fluorine from reacting with

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TABLE II

OXYGEN ANALYSIS OF ORGANOMETALLIC COMPOUNDS

Compound	Empirical formula	Ref	Oxygen, %	
			Calcd	Found
$[\pi\text{-}C_5H_4Si(CH_3)_3]Co[C_4(C_6H_5)_4C(O)]$	$C_{37}H_{33}CoOSi$	*a*	2.76	2.79
$[(\pi\text{-}C_5H_4COOH)Co(\pi\text{-}C_5H_5)]^+B(C_6H_5)_4^-$	$C_{36}H_{32}BCoO_2$	*b*	5.65	5.64
$[(\pi\text{-}C_5H_4NO_2)Co(\pi\text{-}C_5H_5)]^+B(C_6H_5)_4^-$	$C_{34}H_{29}BCoNO_2$	*b*	5.78	5.48
$[\{\pi\text{-}C_5(C_6H_5)_4(OH)\}Co(\pi\text{-}C_5H_5)]^+Br^-$	$C_{34}H_{26}BrCoO$	*b*	2.71	2.70
$[\{\pi\text{-}C_5(C_6H_5)_4(OCOCH_3)\}Co(\pi\text{-}C_5H_5)]^+\text{-}B(C_6H_5)_4^-$	$C_{60}H_{48}BCoO_2$	*b*	3.68	3.68
$[\pi\text{-}C_5H_4(COOCH_3)]_2Ru$	$C_{14}H_{14}O_4Ru$	*c*	18.43	18.41
$[\pi\text{-}C_5H_4(COC_6H_5)]Os(\pi\text{-}C_5H_5)$	$C_{17}H_{14}OOs$	*c*	3.76	3.84
$[C_6H_5C(O)C_6H_5]W(CO)_3$	$C_{16}H_{10}O_4W$	*d*	14.22	14.24
$(C_6H_5)_2P[(\pi\text{-}C_6H_5)Cr(CO)_3]$	$C_{21}H_{15}CrO_3P$	*d*	12.05	12.02
$[(\pi\text{-}C_6H_5)Cr(CO)_3]_2Hg$	$C_{18}H_{10}Cr_2HgO_6$	*d*	15.31	15.37
$(C_6H_5CHO)Cr(CO)_3$	$C_{10}H_6CrO_4$	*e*	26.43	26.34
$[P(C_6H_5)_3]_2Rh(CO)(Cl)$	$C_{37}H_{30}ClOP_2Rh$	*f*	2.64	2.70
$(\pi\text{-}C_5H_5)Rh[C_4(C_6F_5)_4C(O)]$	$C_{34}H_5F_{20}ORh$	*g*	1.75	1.85
$[P(C_6H_5)_3]_2Ir(CO)(Cl)$	$C_{37}H_{30}ClIrOP_2$	*h*	2.05	2.36
$(\pi\text{-}C_5H_5)Ir(CO)_2$	$C_7H_5IrO_2$	*i*	10.21	10.23
$C_6F_5Ti(OC_3H_7)_3$	$C_{15}H_{21}F_5O_3Ti$	*j*	12.24	12.20

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the quartz tube in such a manner as to liberate oxygen during pyrolysis. This preconditioning can best be accomplished by several injections of a hydrocarbon such as isooctane. Also, our method is not applicable to metal oxides which do not decompose thermally below 1050°. With proper care in handling the sample during the weighing process, our method has proven useful for the determination of oxygen in both oxygen- and moisture-sensitive compounds. Several examples are given in Table II.

It is our opinion that the application of this modified Unterzaucher method for the determination of oxygen on a routine basis will greatly increase the usefulness and importance of elemental analyses in determining the chemical composition of new research compounds.

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