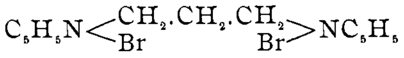
The propane derivative, 

$C_5H_5N{<}\genfrac{}{}{0pt}{}{CH_2.CH_2.CH_2}{Br\qquad\qquad Br}{>}NC_5H_5$

As these results now stand, it appears, *first*, that pyridine is more reactive for addition with diprimary halogen groups than is trimethylamine ; *second*, that with the weaker base the one primary halogen group protects the other from addition when both these groups link together, not when they are separated by a CH_2 group. In this relation it may be noted as a conclusion of Bredig,[1] that in metameric diamines, the bases are stronger, the further removed are the amido groups.

We have studied the reaction of pyridine upon a few primary-secondary dihalogen substituted hydrocarbons, and have not obtained addition in any of these cases. The conditions of addition were digestion in sealed tubes at 80° to 100° C. Propylene bromide, $CH_3.CHBr.CH_2Br$, was treated in several operations, both with di-pyridine proportions and with mono-pyridine proportions, with the result of various products, but without an addition product. Pyridine hydrobromide was at all events obtained. Again, with ethylidine chloride no addition was obtained. Other conditions, however, will be brought to bear upon this class of pyridine additions, in work now in hand in this laboratory.

ANN ARBOR, MICHIGAN.

A PROPOSED SCHEDULE OF ALLOWABLE DIFFERENCE AND OF PROBABLE LIMITS OF ACCURACY IN QUANTITATIVE ANAYSES OF METALLURGICAL MATERIALS.[2]

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WITHIN the past twenty years, metallurgical practice has grown to depend more and more upon a chemical knowledge of the material employed in the various operations. On account of this dependence it has become necessary to have accurate as well as rapid methods for the determination of the elements which take an active part in the different processes.

Many methods for the determination of the various elements

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[1] *Loc. cit.*

[2] Read before the Chemical Section of the American Association for the Advancement of Science, Sept. 2, 1895.

usually met with in metallurgical work have been proposed, each having its own claim for accuracy, or rapidity, or both, but as will be seen from the efforts of the International Committee on the analysis of Iron and Steel, we are far from having perfect methods for metallurgical analysis.

There are many sources of error in ordinary quantitative determinations, which, while they can be partially avoided, can never be wholly overcome. Among these may be mentioned such errors as arise from solubility of precipitates, solubility of apparatus in which operations are performed, impurities in chemicals, inaccurate graduation of volumetric apparatus, unavoidable error in accuracy of weighing, and last, but not least, errors due to what may be termed the personal equation, the presence or absence in the operator of that manipulative skill which distingushes an expert from a clumsy worker. Since we cannot expect absolute agreement in results it may be asked how close should quantitative determinations agree. This question cannot be answered by a single figure since the unavoidable errors in the various determinations differ according to the element determined and the method used in the analysis. Just how great a difference between determinations should be allowed and what the probable limit of accuracy, which may be hoped for, is largely a matter of judgment based upon the examination of the results obtained by different chemists, known to be careful operators, working upon the same material.

Basing our judgment upon the usual errors of analysis, upon the commercial requirements of accuracy and upon the unavoidable sources of error we would propose the following schedule of allowable differences and of probable limits of accuracy for discussion in the section. In the table below the first column shows the element or constituent determined ; the second, a formula for calculating the difference which might be reasonably expected between the results of two chemists working upon the same material and the third column shows a formula for calculating the probable minimum error which may be hoped for. To take an instance : suppose chemist A reports the phosphorus in a specimen of steel as 0.076 per cent, then by the formula in the table we might expect B to report 0.076 ± 0.00352 per cent., and from the third column we could not hope to reduce the error to less than 0.00058 per cent.

Element or constituent.	Allowable difference of per cent.	Probable limit of accuracy.
Iron and Steel.		
Graphitic carbon	$\pm[0.050+(0.02\times Cg)]$	$\pm[0.005+(0.005\times Cg)]$
Cast iron Combined carbon	$\pm[0.050+(0.02\times Cc)]$	$\pm[0.005+(0.005\times Cc)]$
Carbon in steel	$\pm[0.010+(0.02\times C)]$	$\pm[0.002+(0.003\times C)]$
Silicon	$\pm[0.005+(0.02\times Si)]$	$\pm[0.002+(0.003\times Si)]$
Sulphur	$\pm[0.003+(0.03\times S)]$	$\pm[0.0005-(0.005\times S)]$
Phosphorus	$\pm[0.002+(0.02\times P)]$	$\pm[0.0002+(0.005\times P)]$
Manganese in cast iron and steel	$\pm[0.005+(0.04\times Mn)]$	$\pm[0.001+(0.005\times Mn)]$
Manganese in spiegels, ferro, etc.	$\pm[0.050+(0.004\times Mn)]$	$\pm[0.005+(0.001\times Mn)]$
Nickel	$\pm[0.050+(0.02\times Ni)]$	$\pm[0.005+(0.005\times Ni)]$
Ores.		
Silica	$\pm[0.050+(0.006\times SiO_2)]$	$\pm[0.005+(0.001\times SiO_2)]$
Alumina	$\pm[0.030+(0.003\times Al_2O_3)]$	$\pm[0.005+(0.001\times Al_2O_3)]$
Ferric oxide	$\pm[0.030+(0.003\times Fe_2O_3)]$	$\pm[0.005+(0.001\times Fe_2O_3)]$
Iron	$\pm[0.020+(0.003\times Fe)]$	$\pm[0.004+(0.001\times Fe)]$
Manganese	$\pm[0.050+(0.003\times Mn)]$	$\pm[0.005+(0.001\times Mn)]$
Calcium oxide	$\pm[0.050+(0.002+CaO)]$	$\pm[0.010+(0.001\times CaO)]$
Magnesia	$\pm[0.050+(0.010\times MgO)]$	$\pm[0.005+(0.002\times MgO)]$
Phosphorus	$\pm[0.002+(0.02\times P)]$	$\pm[0.0002+(0.005\times P)]$
Phos. pentoxide	$\pm[0.005+(0.02\times P_2O_5)]$	$\pm[0.0005+(0.005\times P_2O_3)]$
Combined water	$\pm[0.050+(0.10\times H_2O)]$	$\pm[0.010+(0.001\times H_2O)]$
Potassium oxide Sodium oxide	$\pm[0.050+(0.020\times K_2O)]$	$\pm[0.005+(0.005\times K_2O)]$
Sulphur in iron ore	$\pm[0.005+(0.030\times S)]$	$\pm[0.001+(0.003\times S)]$
Sulphur in pyrite	$\pm[0.050+(0.004\times S)]$	$\pm[0.005+0.0002\times S)]$
Lead	$\pm[0.050+(0.003\times Pb)]$	$\pm[0.005+(0.0005\times Pb)]$
Zinc	$\pm[0.050+(0.003\times Zn)]$	$\pm[0.005+(0.0005\times Zn)]$
Copper	$\pm[0.030+(0.003\times Cu)]$	$\pm[0.005+(0.001\times Cu)]$
Nickel	$\pm[0.030+(0.003\times Ni)]$	$\pm[0.005+(0.001\times Ni)]$
Arsenic Antimony	$\pm[0.050+(0.010\times As)]$	$\pm[0.002+(0.001\times As)]$
Tin	$\pm[0.010+(0.010\times Sn)]$	$\pm[0.005+(0.001\times Sn)]$.
Coal and Coke.		
Moisture	$\pm[0.050+(0.020\times H_2O)]$	$\pm[0.005+(0.005\times H_2O)]$
Vol. hydrocarbon	$\pm[0.050+(.010\times hydro)]$	$\pm[0.010+(0.001\times hydro)$
Fixed carbon	$\pm[0.050+(0.010\times C)]$	$\pm[0.010+(0.001\times C)]$
Sulphur	$\pm[0.020+(0.030\times S)]$	$\pm[0.005+(0.003\times S)]$
Ash	$\pm[0.050+(0.005\times Ash)]$	$\pm[0.005+(0.001\times Ash)]$
Phosphorus	$\pm[0.002+(0.02\times P)]$	$\pm[0.0002+(0.005\times P)]$