As shown in Table I, the reaction time, while not critical for phenol itself, must be maintained at 25 to 30 seconds for the *o*- and *p*-α-phenylethylphenol and for mixtures of these with phenol. If this is done, results in satisfactory agreement with the calculated values are obtained.

For *p*-cresol, 2-(α-phenylethyl)-*p*-cresol and mixtures of these, conditions essentially identical to those employed for phenol and its alkylated derivatives gave very satisfactory results (Table II). However, when *o*-cresol, 4-(α-phenylethyl-)-*o*-cresol and mixtures of these were analyzed, it was found that a shorter reaction time was necessary in order to obtain reproducible and accurate results. This rapid overbromination of *o*-cresol has also been observed by other investigators (*4*, *5*), but may be successfully overcome by careful control of the reaction time. Lower temperatures may also be helpful (*4*).

This analytical procedure has been successfully applied to analysis of mixtures arising from the alkylation of phenol, *o*-, and *p*-cresol by α-phenyl ethyl chloride, permitting a kinetic study of that reaction (*2*). However, in using the bromination technique for the analysis of phenol mixtures, determinations on mixtures of known compositions must first be made before applying this method to unknown mixtures. It is very likely that this technique cannot be adapted to all phenol mixtures successfully, and experimentation must be undertaken to determine its suitability for each specific case.

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Displacement of the Nitro Group during Determination of Nitrophenols and Nitroanilines by the Koppeschaar Method

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During a study of the determination of 2,4-dinitrophenol and picric acid in mixtures by the Koppeschaar method, it was found that picric acid consumes bromine under the conditions of the procedure and a displacement of the nitro group may occur, rendering the final titration inaccurate. A procedure has been developed in which both phenols are titrated initially and the Koppeschaar method is applied to the titrated liquid to determine 2,4-dinitrophenol; picric acid is calculated by difference.

THE Koppeschaar procedure (*10*), though capable of excellent results with compounds that brominate normally (*5*), is by no means general for the classes named and is subject to errors from several recognized causes. These errors may be due to incomplete bromination because of conflicting directive influences or to the low solubility of the sample or of the partially brominated sample [the latter, in the case of nitrophenols, is the hypobromite compound (*11*)]; oxidation of the sample by bromine or hypobromous acid, as with aniline (*5*) and the nitroresorcinols examined in the present study; bromination of side chains (*15*); displacement of certain nuclear substituents by bromine—e.g., conversion of anthranilic acid and of sulfanilic acid to tribromoaniline (*5*, *8*); and replacement of alcoholic—e.g., hydroxymethyl—groups (*13*). In the course of work on the analysis of mixtures of picric acid and 2,4-dinitrophenol (*16*) it was observed that picric acid, presumably immune to bromination, consumed measurable amounts of bromine if the period of contact exceeded a few minutes, this result being accompanied by a fugitive end point in the final titration with thiosulfate. A similar displacement under preparative conditions—the conversion of picric acid to 6-bromo-2,4-dinitrophenol—was reported by Armstrong (*1*) and by Dhar (*6*). This paper presents the findings of a study of the displacement of the nitro group under the relatively mild conditions of the Koppeschaar analysis.

Of the 18 compounds examined (Table I) all except *o*-nitroaniline, *m*-nitroaniline, the nitroanisoles, and dinitrophenetole were found to consume bromine in excess of that attributable to normal bromination. The nitrophenolic ethers yielded no significant results because of their insolubility in the Koppeschaar liquid. The nitroanilines formed bulky amorphous precipitates that obstructed action of bromine (*5*). The nitroresorcinols consumed abnormally large amounts of bromine owing to oxidation.

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DETECTION OF NITROUS ACID FOLLOWING DISPLACEMENT OF NITRO GROUP BY BROMINE

Preliminary tests showed that the consumption of more than the calculated bromine is associated with the presence of nitrous acid in the liquid; this is detectable by application of the Griess-Ilosvay test, following alkalization of the mixture and acidification with sufficient formic acid to reduce excess bromine and to leave the liquid at an acidity suitable for the diazotization and subsequent coupling.

Attempts to estimate colorimetrically the amount of nitrous acid formed and to correlate this with the excess bromine consumed revealed that the amount of nitrous acid in some cases increased to a maximum and then decreased slightly.

It appears that the momentary concentration of nitrous acid is not a dependable index of the extent of the displacement reaction. Analysis of the reaction liquid for nitrogen (other than nitro nitrogen) by use of Devarda's alloy (*4*) proved to be unfeasible, as this yielded ammonia from picric acid and reduced the nitro group to some extent. To exclude the effect of nitrous acid on the end point of the titration several reagents capable of destroying nitrous acid (urea, sulfamic acid, hydrazine sulfate) were tested, but none was completely effective and all consumed bromine. Analogy with the behaviors of anthranilic acid and sulfanilic acid suggests that displacement of the nitro group is followed by introduction of bromine in its place. Thus far, a number of attempts to isolate and identify such a product (bromodinitrophenol from picric acid or tribromophenol from 2,6-dibromo-4-nitrophenol or from 4,6-dibromo-2-nitrophenol) following prolonged action under the conditions of the Koppeschaar analysis have been unsuccessful. The scantiness of the recovered material and its indefinite character (no increase in bromine and small loss of nitrogen) suggest that action was destructive.

Table I. Effect of Time on Consumption of Bromine by Nitrophenols, Nitroanilines, and Other Compounds[a]

Compound	Atoms of Bromine Consumed per Molecule: 5 min.	20 hr.	167 hr.	Calcd.	Test for HNO_2: 20 hr.	167 hr.
o-Nitrophenol, m.p. 44–45° C.	3.990	4.091	4.209	4	–	+
m-Nitrophenol, m.p. 95–96° C.	5.987	6.027	5.915	6	–	+
p-Nitrophenol, m.p. 112–113° C.	3.941	3.985	4.332	4	Bulky ppt.	+
2,4-Dinitrophenol, m.p. 113–114° C.	2.003	2.124	2.723	2		+
Picric acid, m.p. 120–121° C.	0.0309	(1.504 22 hr.)	3.937	0	+	+
o-Nitroaniline, m.p. 70–71° C.	3.978 (3.974 30 min.)	3.981	3.606	4	Bulky ppt.	
m-Nitroaniline, m.p. 110–111° C.	5.977	5.977	5.477	6	Bulky ppt.	
p-Nitrodimethylaniline, m.p. 161–162° C.	4.020	6.741	9.325	4	+	+
2,6-Dibromo-4-nitrophenol, m.p. 143–144° C.	0.0443	1.489	8.097	0	+	+
4,6-Dinitro-*o*-cresol, m.p. 85–86° C.	0.011 0.055	4.785	...	0	+	
2,4-Dinitro-1-naphthol, m.p. 81–82° C.	0.292	1.374	3.491	0	+	+
2-Nitroresorcinol, m.p. 81–82° C.	10.008	12.143	14.042	4	+ (+ in 5 min.)	+
2,4-Dinitroresorcinol, m.p. 160° C.	0.647 (0.704 10 min.)	11.680 (11.222 11 hr.)	... 9.642		+ +	+
2,4,6-Trinitroresorcinol, m.p. 177–178° C.	0.522 (1.922 30 min.)	(6.559, 11 hr.) (8.43 22 hr.)	... 5.203		(+ in 30 min.)	
2,4-Dinitrothymol, m.p. 53–54° C.	0					
2,4-Dinitroanisole, m.p. 94–95° C.	Insoluble, bromination slight					
2,4,6-Trinitroanisole, m.p. 67–68° C.	Insoluble, bromination slight					
2,4-Dinitrophenetole, m.p. 85–86° C.	Insoluble, bromination slight					

[a] Temperature 20–25° C.; samples 0.09–0.15 gram.

Table II. Effects of Temperature and Time on Bromination of Nitrophenols

Compound	Temp., ° C.	Atoms Bromine Consumed per Molecule: 5 min.	10 hr.	20 hr.	Calcd.
o-Nitrophenol	0–5	...	...	3.921	4
	5–10	3.935	3.981	...	
	20–25	3.990	...	4.091	
	25–30	4.004	4.035	4.209	
m-Nitrophenol	0–5	...	...	5.905	6
	5–10	5.914	5.959	...	
	20–25	5.987	...	...	
	25–30	5.987	5.990	...	
p-Nitrophenol	0–5	...	...	3.964	4
	5–10	3.965	3.968	...	
	20–25	3.941	...	...	
	25–30	4.004	4.002	...	
2,4-Dinitropheno	0–5	...	...	2.006	2
	5–10	...	1.989	...	
	20–25	2.003	...	2.124	
	25–30	2.003	2.137	2.121	
Picric acid	0–5	...	...	0.1617	0
	5–10	0.0236	0.1338	...	
	25–30	0.0309	0.6989	1.465	
2-Nitroresorcinol	5–10	...	8.463	8.611	4
	20–22	...	8.658	...	
2,4-Dinitroresorcinol	5–10	...	9.262	...	2
	20–22	...	11.222	...	
2,4,6-Trinitroresorcinol	5–10	...	4.035	6.490	0
	20–22	...	6.559		

INFLUENCE OF EXPERIMENTAL CONDITIONS ON KOPPESCHAAR BROMINATION

Effect of Time. Normal bromination is rapid, and because the effects of the displacement reaction may not become apparent in the usually brief bromination periods, it is clear that this reaction is relatively slow. Table I presents the results of experiments to test the effect of time upon the two reactions.

Except for *o*- and *m*-nitroanilines, the amount of bromine consumed increases with time and, even with some compounds which can be accurately determined by brief bromination, at some point exceeds the theoretical [especially *o*- and *p*-nitrophenols, 2,4-dinitrophenol, and *p*-nitrodimethylaniline (*8*)]. Several compounds (picric acid, 2,6-dibromo-4-nitrophenol, 2,4-dinitronaphthol, and 4,6-dinitro-*o*-cresol) not capable of normal bromination consume bromine in amounts that increase markedly with time, though the amounts consumed in 5 minutes are small. Prolonging the bromination period does not improve results by the Koppeschaar method when applied to nitro compounds and may vitiate them. The rapid and excessive consumption of bromine by dinitro-*o*-cresol, 2,4-dinitrothymol, and especially the several nitroresorcinols, is attributable to oxidation.

Effect of Temperature. Table II records the results for eight nitrophenols, showing the combined effects of temperature and time.

The effect of increasing time and temperature upon the bromination of nitrophenols is toward consumption of more than the theoretical amount of bromine. In Table II the separate effects of the two variables can be seen by comparing the results horizontally or vertically. Bromination of the isomeric nitrophenols and of 2,4-dinitrophenol is substantially normal up to room temperature, if the time of contact is brief. Of the four compounds referred to, *o*-nitrophenol and 2,4-dinitrophenol, show abnormality for periods of 10 hours or more at 25° to 30° C. The results for picric acid indicate that to restrain attack by bromine so that it is negligible contact should be brief and below room temperature. The results for the nitroresorcinols show, for both time and temperature, pronounced effects that suggest concurrent bromination, displacement of the nitro group, and oxidation; these results have no analytical significance.

Effect of Acidity. Table III presents the results of experiments in which the quantity of hydrochloric acid was varied from somewhat less than the usual amount to four times the usual amount.

The results indicate that for brief periods of bromination the amount of acid used in the standard procedure (5 ml. of concentrated acid in a total volume of 80 ml.) is satisfactory, and that increasing acidity retards somewhat both normal bromination and displacement of the nitro group. The two effects are of

Table III. Effect of Acid Concentration on Bromination of Nitrophenols

Compound	Concd. HCl, Ml.	Atoms of Bromine Consumed per Molecule: 5 min.	20 hr.	Calcd.
o-Nitrophenol	3	3.957	5.009	4
	5	4.004	4.691	
	10	3.964	4.265	
	20	3.909	4.095	
m-Nitrophenol	3	5.951	5.972	6
	5	5.987	5.859	
	10	5.864	5.941	
	20	5.854	...	
p-Nitrophenol	3	3.987	3.970	4
	5	4.004	3.980	
	10	3.940	3.900	
	20	3.840	3.779	
2,4-Dinitrophenol	3	1.968	2.295	2
	5	2.003	2.121	
	10	1.971	1.995	
	20	1.930	1.929	
Picric acid	3	0.1003	1.973	0
	5	0.0309	1.465	0
	10	...	0.638	
	20	...	0.059	

Table IV. Effect of Amount of Bromine upon Bromination of Nitrophenols[a]

Compound	Bromine Taken (1 = Usual Amt.)[b]	Atoms of Bromine Consumed per Molecule: 5 min.	20 hr.	Calcd.
o-Nitrophenol	1.0	4.004	...	4
	1.4	3.998	4.687	
m-Nitrophenol	1.0	5.987	...	6
	1.4	5.959	5.961	
p-Nitrophenol	1.0	4.004	...	4
	1.4	3.992	4.015	
2,4-Dinitrophenol	1.0	2.005	...	2
	1.4	1.994	2.149	
Picric acid	1.0	0.0309	...	
	1.4	0.0309	1.404	

[a] Temperature 25–30° C.
[b] Bromine from 25 ml. of 0.1*N* Koppeschaar solution.

about the same magnitude, so that one cannot expect control of acidity to exclude the displacement reaction while permitting normal bromination. The influence of acidity is most strikingly shown by the 20-hour results for picric acid: A sevenfold increase in acid decreases the displacement reaction about 97%.

Effect of Amount of Bromine. The results of experiments in which the amounts of Koppeschaar solution were varied from the usual amount (about twice the theoretical) to 40% more appear in Table IV.

The effect of change in the amount of bromine is slight, especially for the 20-hour trials; the influence of time exceeds that of amount of bromine. These results, together with visual observation, suggest that the amount of bromine ordinarily used maintains virtual saturation with respect to bromine, and that increase in its amount does not much increase its effective concentration.

Chemistry of Displacement Reaction. The displacement of the nitro group by aqueous bromine may be attributed to free bromine or to hypobromous acid or both:

$$ArNO_2 + Br_2 \rightarrow ArBr + BrNO_2$$
[hypothetical nitroxyl bromide (*4*)] (1)
$$BrNO_2 + H_2O \rightarrow HBr + HNO_3$$

$$Br_2 + H_2O \rightarrow HOBr + HBr$$
$$ArNO_2 + HOBr \rightarrow ArBr + HNO_3 \quad (2)$$

The ability of free bromine to effect this replacement appears to be established (*1, 3, 6, 17*); that of hypobromous acid to do so was ascertained experimentally. It was found that, following contact of aqueous hypobromous acid with the isomeric nitrophenols or with picric acid, the liquids contained nitrous acid. In several cases precipitates appeared; analysis of one of these showed it contained mercury, indicating mercuration by the mercuric bromide present in the reagent as prepared by the Balard method (*2*). Separate experiments showed that mercuric bromide alone is not able to displace the nitro group from the same nitrophenols.

The primary displacement product is probably nitric acid, and its conversion to nitrous acid appears to be inevitable because of interaction with hydrobromic acid which is present in abundance.

$$2HNO_3 + 6HBr \rightarrow 3Br_2 + 2NO + 4H_2O \quad (3)$$

The nitric oxide thus produced may react with bromine to form nitrosyl bromide and then nitrous acid and hydrobromic acid:

$$2NO + Br_2 \rightarrow 2NOBr$$
$$2NOBr + H_2O \rightarrow HNO_2 + HBr \quad (4)$$

or with air (oxygen) to yield nitrogen dioxide, which with water yields nitrous and nitric acids:

$$2NO_2 + O_2 \rightarrow 2NO_2$$
$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \quad (5)$$

or with nitric acid to yield nitrous acid:

$$2NO + HNO_3 + H_2O \rightarrow 3HNO_2 \quad (6)$$

Nitrous acid formed by Reactions 4 and 6 may be oxidized to nitric acid by hypobromous acid, or by bromine water, or by air:

$$HNO_2 + HOBr \rightarrow HNO_3 + HBr \quad (7)$$

$$2HNO_2 + Br_2 + 2H_2O \rightarrow 2HNO_3 + 2HBr \quad (8)$$

$$2HNO_2 + O_2 \rightarrow 2HNO_3 \quad (9)$$

To test the extent to which oxygen may be involved (Equations 5 and 9) experiments were performed with air displaced from the liquid and the space above it by nitrogen or carbon dioxide. These showed that picric acid consumed less bromine in absence of air than in its presence (in 22 hours 0.994 atom *vs.* 1.504 atoms, respectively). It may be assumed that little or no oxygen is formed by the reaction $2HOBr \rightarrow 2HBr + O_2$, as light is excluded during the Koppeschaar analysis and the amount of hypobromous acid momentarily present is probably small. Further, the final result of action of oxygen is the formation of nitrous and nitric acids and not an increase in the bromine consumed. Reactions 9 and 8 (which consume, respectively, oxygen and bromine to oxidize nitrous acid) are in competition, with an enormous statistical advantage for Reaction 8. The nitric acid formed is thereafter involved with hydrobromic acid (Reaction 3) to yield ultimately both nitrous and nitric acids and to regenerate bromine.

Table V. Effects of Temperature, Time, and Acidity on Determination of 2,4-Dinitrophenol in Presence of Picric Acid

Sample Mixture	Temp., ° C.	Time, Min.	Concd. HCl, Ml.	Atoms Br Consumed	Indicated Purity of DNP, %
2,4-Dinitrophenol, 0.08030 gram	20–25	5	5	2.050	102.5
		30	5	2.023	101.2
Picric acid, 0.03024 gram		60	5	2.022	101.1
		5	10	2.043	102.2
		30	10	2.023	101.2
		60	10	1.964	98.2
		5	20	2.012	100.6
		30	20	1.992	99.6
		60	20	1.960	98.0
2,4-Dinitrophenol, 0.09034 gram	0–10	5	5	1.987	99.4
		30	5	1.988	99.4
Picric acid, 0.03564 gram		60	5	1.995	99.8
		5	10	1.983	99.2
		30	10	1.988	99.4
		60	10	1.988	99.4
		5	20	1.964	98.2
		30	20	1.983	99.2
		60	20	1.983	99.2

The system contains, or by primary or secondary reactions produces, a group of incompatible substances, and after a lapse of sufficient time it may reach an apparently steady state that represents a balance among a number of interdependent reactions, with the reactants either in a condition of interlocking equilibria or at concentrations below the threshhold values for reaction. At any moment there could then be present bromine, hypobromous acid, hydrobromic acid, nitric acid, nitrous acid, and nitric oxide, and this conclusion may account for the apparently paradoxical facts: nitrous acid is present after prolonged periods of time during which free bromine has been continuously present, and in some brominations—e.g., of *m*-nitrophenol and *m*-nitroaniline—the total apparent consumption of bromine may, beyond a certain point, show a decrease with time. The possibility that adding formic acid before the test for nitrous acid may cause reduction of nitric to nitrous acid was excluded by the inability of formic acid to effect this reduction at low concentration. It is possible that no nitrous acid persists so long as an excess of bromine is present, but that following its reduction by formic acid some nitrous acid is formed and survives.

When displacement of the nitro group occurs it is doubtful that results by the Koppeschaar method are trustworthy, owing

to the secondary reactions mentioned. Reaction 3 produces free bromine while Reactions 1, 2, 4, and 8 consume bromine. The bromine liberated in Reaction 3 may exceed the bromine consumed to effect displacement of the nitro group. All that can be determined in the Koppeschaar analysis is the over-all total amount of bromine consumed, and there is no measurable and unique criterion of the extent of the displacement reaction. Following the displacement reaction there exists a situation that cannot be delt with using only the analytical data; it is aggravated by the fugitive nature of the end point, which is presumably already delayed on its first appearance.

Table VI. Analyses of Mixtures of 2,4-Dinitrophenol and Picric Acid[a]

Mixtures Analyzed	Wt., Gram	%	Found Gram	Found %
DNP	0.3326	100.0	0.3332	100.18
PA	0.0000	0.0	0.00	0.00
DNP	0.3346	98.35	0.3336	98.71
PA	0.0056	1.65	0.0044	1.29
DNP	0.3108	86.81	0.3114	86.91
PA	0.0472	13.19	0.0469	13.09
DNP	0.2608	85.34	0.2609	85.23
PA	0.0448	14.66	0.0452	14.77
DNP	0.2358	76.85	0.2358	76.83
PA	0.0710	23.15	0.0711	23.17
DNP	0.1566	50.16	0.1572	50.14
PA	0.1556	49.84	0.1563	49.86
DNP	0.1244	31.12	0.1255	31.87
PA	0.2754	68.88	0.2683	68.13
DNP	0.0711	24.09	0.0713	24.31
PA	0.2240	75.91	0.2220	75.69
DNP	0.0590	15.73	0.0557	15.86
PA	0.3162	84.27	0.2957	84.14
DNP	0.0264	8.32	0.0265	8.27
PA	0.2912	91.68	0.2942	91.73
DNP[b]	0.0142	3.60	0.0195	2.50
PA	0.3808	96.40	0.3606	97.50
DNP	0.0000	0.00	0.0000	0.00
PA	0.1908	100.00	0.1911	100.15

[a] Temperature 20–25°; time 30 minutes; concentrated hydrochloric acid, 5 ml.
[b] Three other analyses of mixtures in this range gave poor results, indicating interference by picric acid when present to the extent of about 95% or more.

ANALYTICAL APPLICATION OF FINDINGS

Analysis of Mixtures of 2,4-Dinitrophenol and Picric Acid. In the light of the disclosures outlined above, the method for analysis of mixtures of dinitrophenol and picric acid was improved to a state of usefulness. The need for a method to estimate 2,4-dinitrophenol and picric acid when present in mixtures arose during work on the oxynitration process for preparation of picric acid from benzene by a research team at the University of Pennsylvania during World War II. The product consists largely of dinitrophenol, with some picric acid, and the amount of the former must be known in order both to judge the effectiveness of the oxynitration and to calculate the amount of 98% nitric acid required for nitration of dinitrophenol to picric acid. This preliminary work disclosed the fact that picric acid consumes bromine under the conditions of the Koppeschaar analysis at a rate affected by both time and temperature, and led to the further study reported in this paper.

The effects of time, temperature, and acidity upon the bromination of mixtures of the two compounds were determined, and the results (Table V) were used to assist in the selection of conditions that would permit quantitative determination of dinitrophenol by the Koppeschaar method with minimal, or at most tolerable, interference by picric acid.

The effects of temperature and time are seen to exceed that of acidity; at 0° to 10° C. interference by picric acid is negligible and results for dinitrophenol are reasonably good, with only slight decrease in dinitrophenol values at higher acidities. As a compromise in the interest of convenience it was decided to operate at room temperature (20° to 25° C.) and at the usual acidity and to omit replacement of air by inert gas, with the bromination period reduced to 30 minutes or less. The entire analytical procedure involves an initial acidimetric titration of both phenols and application to the titrated liquid of the Koppeschaar method to determine dinitrophenol; picric acid is calculated by difference. Test results for the procedure appear in Table VI.

EXPERIMENTAL

The compounds examined are listed in Table I. All were purified to constant melting points, *o*-nitrophenol by steam distillation and the others by recrystallization: *o*-nitroaniline from water, picric acid and 2,4,6-trinitroresorcinol from water containing hydrochloric acid, and the others from aqueous alcohol. The melting points appear in Table I. Each value listed in Tables I to V represents the average of two determinations. Each value listed in Table VI represents the average of three determinations.

The Koppeschaar solutions were 0.1N with respect to available bromine: potassium bromide, 50.0 grams; potassium bromate, 2.8 grams per liter. The 0.1N thiosulfate solutions were standardized weekly against potassium iodate (*12*). Extended brominations were effected in specially made, thin-walled glass ampoules of about 100-ml. capacity, each with two concavities pushed into the wall (to facilitate crushing the ampoule under water); an 8-mm. tubular side arm permitted introduction of liquids through an improvised funnel tube with semicapillary stem, drawn from a thistle tube. After charging, the ampoule was closed by sealing off the neck while the ampoule was being cooled in an ice bath. For briefer brominations there were used 500-ml. iodine flasks with stoppers of tested tightness.

General Procedure for Bromination. Samples were taken as 25-ml. aliquots of solutions of the compounds in water or dilute sodium hydroxide. To the sample, in a 500-ml. iodine flask or in the glass ampoule, were added 25 ml. of water, 25 ml. (from a pipet) of 0.1N Koppeschaar solution, and finally, without agitation, 5 ml. of concentrated hydrochloric acid. The flask was stoppered, or the ampoule was sealed, at once. The amount of sample in each case was such that the Koppeschaar solution taken would provide approximately a 100% excess of bromine over that calculated for normal bromination. The flask or ampoule was allowed to stand in the dark at the temperature and for the period specified.

Analyses in iodine flasks were completed in the usual manner, using 5 ml. of 40% potassium iodide solution for combining the free bromine, after which the equivalent iodine was titrated with 0.1N thiosulfate using 5 ml. of 1% soluble starch solution added near the end point. Analyses in sealed ampoules were completed by immersing the ampoule in 150 ml. of 10% potassium iodide solution and by breaking it by pressure with a heavy glass rod applied at one of the thin-walled concavities. The operations following introduction of potassium iodide were completed without interruption, and the titration was completed rapidly, as displacement of the nitro group led to delayed liberation of iodine and to reappearance of the starch-iodine color after the first end point was reached. With each series a blank analysis (25 ml. of Koppeschaar solution, 50 ml. of water, and 5 ml. of concentrated hydrochloric acid) was run, to determine the value of the Koppeschaar solution in terms of equivalent standard thiosulfate.

Results stated as "atoms of bromine consumed" in the tables are calculated thus:

$$\text{Atoms of bromine per molecule of sample} = \frac{(V - V_1) \times \text{mol. wt.} \times 0.001N}{S}$$

in which V is milliliters of thiosulfate used in the blank titration, V_1 is milliliters of thiosulfate used in the main titration, N is the normality of the thiosulfate, and S is the weight of sample in grams. Results stated in terms of per cent purity are calculated as 100 times the quotient of the number of atoms of bromine consumed per molecule of sample divided by the theoretical number of atoms of bromine.

Identification of Nitrous Acid Following Displacement of Nitro Group. The analysis liquid, at the end of the bromination period, was neutralized by addition of 25% sodium hydroxide solution, and was then reacidified by addition of 3% formic acid until pH was about 3. The formic acid first liberated the bromine combined by the alkali and then reduced it. To the prepared solution were added 1 ml. of 0.5% 1-naphthylamine in 30% acetic acid and, after 2 minutes, 1 ml. of 1% sulfanilic acid solution prepared as directed by Snell and Biffen (*14*). For each series a blank analysis was similarly treated. In presence of nitrous acid a violet-pink color appeared within a few minutes, the intensity increasing for about an hour. This test gave negative results

following normal brominations of nitrophenols, but positive results when excessive bromine was consumed and the end points were impermanent.

Influence of Experimental Conditions and Structure. In all experiments the standard procedure was changed only to the extent required to ascertain the effects of changes in the variable(s) under study. Brominations continued for 167 hours were effected in sealed glass ampoules. Temperatures above or below room temperature were maintained by keeping the iodine flasks or ampoules in a constant-temperature oven or in a refrigerator, with periodic inspections. Variations in acidity were made at constant volume by reciprocal adjustments of the amounts of water and hydrochloric acid added. Variations in the amounts of bromine were made at constant volume by compensating adjustments of the amounts of Koppeschaar solution and water. The results of the tests appear in Tables I, II, III, and IV.

Action of Hypobromous Acid on Nitrophenols. An aqueous solution of hypobromous acid was prepared by the method of Balard (*2*); the brown-red solution was filtered from the solid residue and was extracted several times with carbon tetrachloride and finally with ether to remove free bromine. This reagent contains hypobromous acid and mercury(II) bromide:

$$HgO + 2Br_2 \rightarrow 2HOBr + HgBr_2$$

To test the action of hypobromous acid upon nitrophenols, 25 ml. of the colorless or straw-colored reagent was added to a 25-ml. aliquot of a solution of *o*- or *p*-nitrophenol or of picric acid for periods from 1 to 20 hours. In all cases, positive tests for nitrous acid were obtained by the test procedure described. Both mononitrophenols yielded precipitates during contact with the reagent; one of these precipitates was removed and washed, and analysis proved it contained mercury. The possibility that the nitro group might be replaced by mercuration (rather than by action of hypobromous acid) was excluded by tests in which the nitrophenols (25-ml. aliquots) were treated with saturated aqueous mercuric bromide (25 ml.) and concentrated hydrobromic acid (2 ml.) for 1 to 20 hours, after which the liquids were tested for nitrous acid with negative results.

In separate tests it was found that the normal Koppeschaar bromination is not noticeably accelerated or retarded by presence of mercuric bromide. Samples of *o*- and *p*-nitrophenol, brominated for 5 to 30 minutes at 20° to 25° C. in presence of 25 ml. of saturated aqueous mercuric bromide, yielded 100.05 and 99.92%, respectively, comparing well with the results by the usual procedure (*5*).

Experiments that resulted indecisively and are not described here (*9*) include the colorimetric determination of nitrous acid formed in the displacement reaction, the attempted determination of nitrogen other than nitro nitrogen in the analysis liquid by use of Devarda's alloy (*4*), attempts to destroy nitrous acid prior to the titration (using urea, hydrazine sulfate, or sulfamic acid), and attempts to prove the replacement of nitrogen dioxide by bromine by isolation and identification of the brominated product.

Determination of 2,4-Dinitrophenol and Picric Acid in Admixture. The procedure consists of two operations performed on the same sample: determination of total acidity by titration with standard alkali and Koppeschaar analysis of the resulting solution under conditions such as to minimize involvement of picric acid. The bromine consumed is calculated to dinitrophenol, and picric acid is calculated by difference. The samples, in 500-ml. iodine flasks, were first dissolved by addition (from a buret) of a slight excess of 0.1*N* sodium hydroxide (standardized against 99.95% picric acid, using phenolphthalein indicator), after which a small excess of 0.1*N* acid was added (from a buret) and the titration was completed with 0.1*N* alkali using phenolphthalein indicator. For reproducibility and certainty the titrations were continued to a rather deep color, which was compensated in the standardizations in which like volumes and procedure were used. To the titrated and nearly neutral solution was added 25 ml. of 0.1*N* Koppeschaar solution followed by 5 ml. of concentrated hydrochloric acid, and analyses were completed by the general procedure.

The results of preliminary trials to determine favorable conditions with respect to temperature, time, and acidity appear in Table V. In consideration of the findings and as a compromise between optimum conditions and convenience, it was decided to operate at 20° to 25° C., to use 5 ml. of concentrated hydrochloric acid, and to continue bromination for 30 minutes. This procedure, applied to mixtures of dinitrophenol and picric acid over a wide range of compositions, yielded the results collected into Table VI, which indicate that satisfactory analysis is possible with mixtures containing at least 25% dinitrophenol.

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Zinc Mercurithiocyanate Method and Its Application to Yellow-Metal Alloys

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The results of over 80 student analyses for zinc on 26 different alloys, containing from 0.3 to 23% of zinc, are reported. A comparison of these results by the mercurithiocyanate method with others obtained by the classical pyrophosphate procedure shows a definite superiority for the former method from the standpoints of precision and accuracy. The selectivity is also improved—iron, for example, need not be removed. The time for analysis is approximately one half of that for the phosphate method. Some misconceptions in the literature are mentioned.

THE mercurithiocyanate method for the determination of zinc was first investigated by Lundell and Bee (*6*). They advocated solutions of 5% acidity. Large amounts of salts (potassium sulfate, ammonium acetate, ammonium thiocyanate) were shown to give high results. Their factor of 0.1266 for converting the weight of precipitate to a weight of zinc was based upon the assumption that the monohydrate prevailed on drying at 102° to 108° C. Later, Jamieson (*5*) showed that the precipitate was anhydrous and that the gravimetric factor must therefore be 0.1312. The interferences of arsenic(III) and small amounts of nickel were shown to be negligible. Jamieson (*5*),