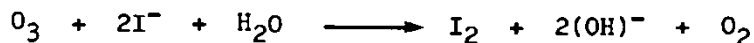


DETERMINATION OF OZONE IN WATER

In order to obtain proper disinfection of waters, it is necessary to introduce a dosage of ozone such that the residual ozone at the exit of the contact towers must be greater than 0.4 mg/L. It is thus necessary to have available a method for ozone analysis in water which is very sensitive between 0 and 1.5 mg/L for ozone.

In the absence of all other oxidants, the iodometric method remains the most often used procedure. It is based on the ability of ozone to displace iodine from alkaline iodide solutions according to the equation:



In our laboratories, we determine residual ozone in water by iodometry. The liberated iodine is reduced by a standard solution of N/24 arsenite in solution buffered by sodium bicarbonate. This method is not very precise, since the determination of the end point, turning from blue to colorless, is delicate and requires excellent perception by the technician.

In the presence of chlorine and of ozone, the iodometric method does not allow differentiation of the two oxidants and determines total oxidants instead. In the course of the study on the influence of ozone on the chlorine demand of water, syringaldazine has been shown to be a very sensitive reagent to iodine and, with an addition of glycine (5), permits differentiating between the two oxidants in admixture.

We will present here the single determination of ozone by syringaldazine.

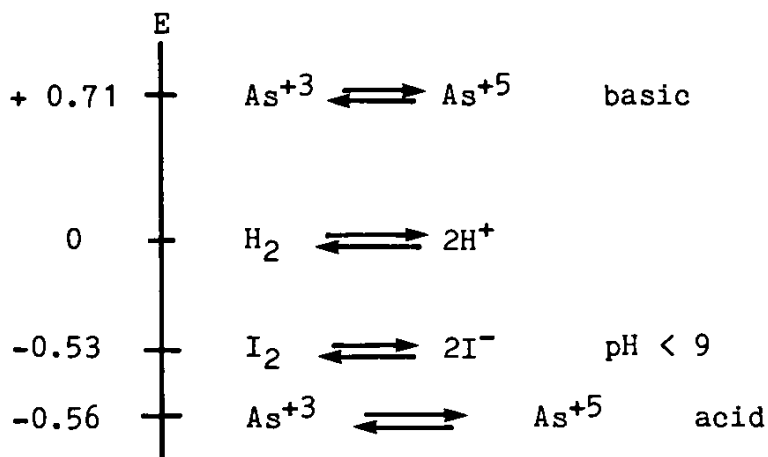
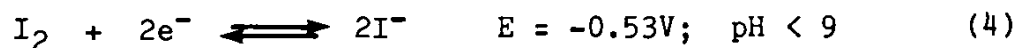
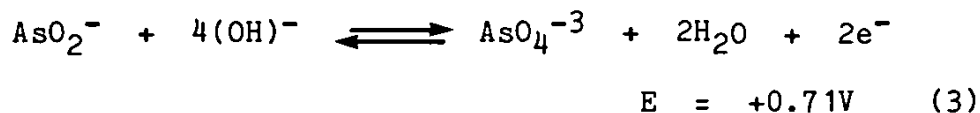
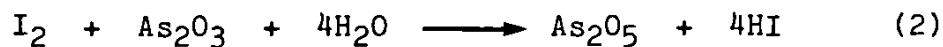
DETERMINATION OF OZONE IN WATER AND AIR

TABLE II. PRINCIPLE OF THE IODINE-ARSENITE METHOD

1) **Action of Ozone**



2) **Reduction of Iodide by Arsenite**



Determination of Ozone by Syringaldazine

Syringaldazine is, from the outset, a reagent for free chlorine (6), which develops a very intense rose coloration with iodine according to the reaction shown in Figure 4. The absorption maximum is situated at 585 nm (Figure 5).

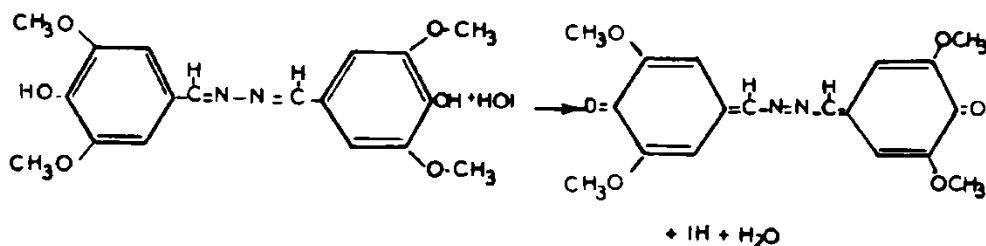


Figure 4. Reaction of hypiodous acid (HOI) on syringaldazine.

When one considers that one mole of ozone liberates one mole of iodine, it is possible to establish, as has Schechter (7), an absolute ozone standardization starting from a standard solution of triiodide buffered at pH = 7. For the establishment of the standardization curve, the following equivalence is taken into account:

$$1 \text{ mL of } 0.01N \text{ iodine solution} = 0.24 \text{ mg of ozone.}$$

Figure 6 shows the standardization curve which relates the theoretical ozone dosage to the optical density measured with an Acta III Beckmann spectrophotometer after reaction of standard solutions of 0.008% syringaldazine triiodide in alcoholic solution. This spectrophotometric method allows determination of levels of ozone between 0.04 and 1.4 mg/L of ozone.

For doses of ozone higher than 1.4 mg/L, one observes a color change from the rose-violet tint to orange, with precipitation of flocculated iodine. It is always possible to determine higher ozone concentrations, upon prior dilution of the sample of liberated iodine. The operational mode of this method is very simple: it suffices to introduce in a Nessler tube previously washed with ozone and heated at 140°C, 1 g of potassium iodide and 50 mL of ozonized water. The solution is agitated and 5 mL of syringaldazine reagent is introduced -- spectrophotometric readings are made between 1 and 1.5 minutes later.

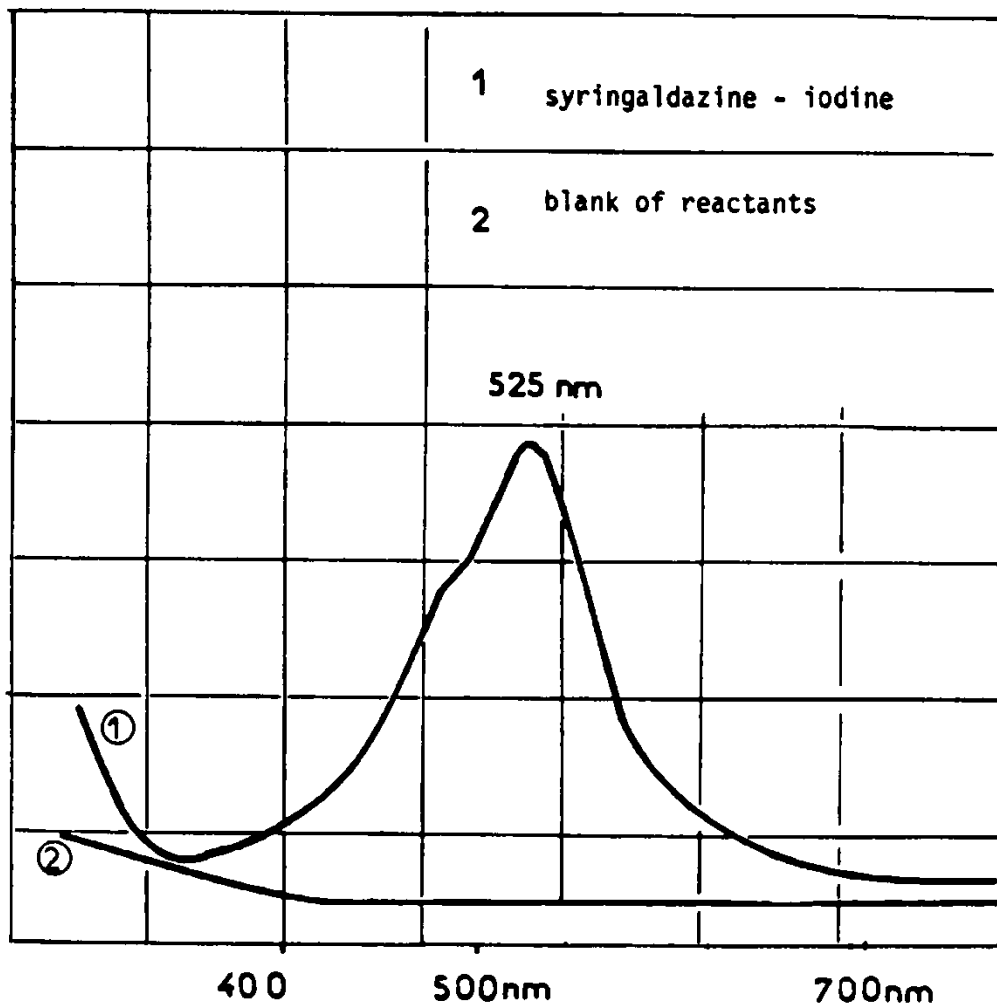


Figure 5. Absorption spectra of syringaldazine in the presence of iodine (Acta III Beckmann spectrophotometer).

Comparison of the Two Methods

In a first stage, one introduces triiodide solutions into distilled water, in which verification titrations have been made by the two methods. One observes that the two methods are practically equivalent, the ratio between the measurements is about 1.03, within the experimental errors of each of the methods (see Table VI).

One then introduces known doses of ozone in water. After a six minute agitation time, the ozone is displaced by addition of potassium iodide and the iodine liberated is determined by the two methods (see Table VII).

TABLE VI. COMPARISON OF THE METHODS OF DETERMINATION OF IODINE BY SODIUM ARSENITE AND BY SYRINGALDAZINE. ADDITION OF IODINE IN DISTILLED WATER

mg/L of ozone introduced in form of iodine	ozone recovered, mg/L		ratio S/A
	arsenite N/24	syring- aldazine	
0.43	0.42	0.432	1.042
0.24	0.242	0.25	1.033
0.96	0.94	0.97	1.032

TABLE VII. COMPARISON OF METHODS OF DETERMINATION OF OZONE IN WATER BY LIBERATION OF IODINE AND DETERMINATION OF SYRINGALDAZINE OR ARSENITE

Syringaldazine Method (S)	Arsenite Method (A)	ratio of S/A
0.97	0.84	1.15
0.12	0.095	1.26
0.7	0.57	1.22
2.34	1.84	1.27
1.25	1	1.25
0.2	0.145	1.37
0.23	0.18	1.27
0.23	0.22	1.05
0.34	0.245	1.38
0.44	0.38	1.15
0.625	0.5	1.25
0.75	0.685	1.1
0.9	0.8	1.12

* The concentrations of ozone are expressed in mg/L.

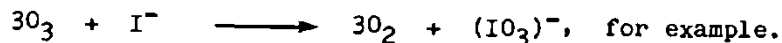
automation of ozone contacting, it is of great interest that the technique be capable of a rapid response and that the apparatus be capable of continuous operation.

IODOMETRIC AND RELATED TECHNIQUES

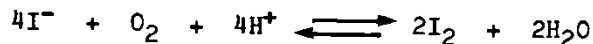
Iodometry still constitutes practically the sole absolute method for determination of dissolved ozone. The principal reaction is the following:



However (1,3), in alkaline medium competitive reactions can appear:



It is known that ozone is unstable in alkaline solution. Results obtained in alkaline medium are, consequently, by default (5). In acid medium, oxygen is capable of oxidizing iodide according to the reaction:



The importance of pH control also should be understood. The fundamental reactant is neutral KI obtained by dissolution in a mixture 0.1M in disodium phosphate and 0.1M in monopotassium phosphate.

The concentration of KI solutions varies between 2 and 5%. The most concentrated solutions are indicated for determination of the weakest ozone residual concentrations (4).

DETERMINATION OF OZONE AND CHLORINE DIOXIDE IN WATER BY THE INDIGO METHOD

Jürg Hoigné and Heinz Bader

SUMMARY

The Indigo Method is well-known for the measurement of ozone in air and exhaust gases. It has now been adapted for the measurement of ozone and chlorine dioxide in drinking water and in other aqueous solutions. This method is faster and of higher precision than the colorimetric methods which are generally applied in waterworks. In the pH region ≤ 4 , one mole of ozone decolorizes 1.0 mole of aqueous sulfonated indigo. The stoichiometric factor stays constant even if concentrations varied in the range from 5 $\mu\text{g/L}$ to 10 mg/L . The absorbance at 600 nm changes by $\sim 20,000$ when based on an addition of 1 mol/L ozone and a 1 cm cell.

Chlorine dioxide is determined at pH > 4 . The absorbance changes by $\sim 7,000 - 9,000$ per 1 mol/L of added chlorine dioxide.

All calibration curves are linear. Reagents and oxidized reagents are quite stable. Hydrogen peroxide, organic peroxides, chlorite, chlorate, manganous ions and oxidized species in drinking water do not interfere with the determination. Chlorine is masked by malonic acid or glycine when ozone or chlorine dioxide are to be determined. Good photometers give a precision of 1.5%, or 2 $\mu\text{g/L}$. Visual methods have a limit of detection of about 10 $\mu\text{g/L}$.

INTRODUCTION

Many methods have been described in the literature for determination of ozone and chlorine dioxide. For our kinetic measurements in natural water and model solutions, however, we could not find adequate instructions. We have therefore adapted the indigo method for determination of ozone and chlorine dioxide in water solutions. This method is based on the fact that 1 mole of ozone or 2 to 3 moles of chlorine dioxide decolorizes 1 mole of blue dye in an extremely fast reaction.

Translated from *Vom Wasser* 55:261-280 (1980), with permission from V.C.H. Verlagsgesellschaft mbH, Pappelallee 3, Postfach 1260, 6940 Weinheim, BRD.

In the course of our earlier work (1,2), we found that the sulfonated form of indigo showed some notable qualities which make it attractive for routine analysis of ozone or chlorine dioxide in different types of drinking water:

1. Indigo trisulfonate and indigo disulfonate are commercially available in calcium and sodium forms as redox and/or pH indicators. The purity of these products is sufficient for the preparation of reagent solutions.
2. Sulfonated indigo is very soluble in water; concentrated stock solutions are easily prepared, and the dye shows no tendency to affect the measurements through absorption processes, as do some water contaminants.
3. Indigo reagent stock solutions keep for months when stored in a dark place and at low pH.
4. Indigo trisulfonate and indigo disulfonate absorb at 600 and 610 nm, with relatively high molar absorption coefficients of about 20,000 L/(mol-cm) (3) (see Figures 1 and 2). Intrinsic colors of natural waters do not interfere in this spectral range. Photometers, and even the human eye, have a good degree of accuracy in this range.
5. The absorption changes with the dosage of the oxidizing agent at each wavelength in the range of the absorption band (ca 550 to 650 nm) in a strictly linear fashion. In the case of the action of ozone and chlorine dioxide, only products which do not have absorptions in the visible spectrum occur (4,5).
6. An indigo molecule has only one functional group with which the ozone or chlorine dioxide reacts quickly. This is the $-C=C-$ double bond, which contributes the chromophoric structure to indigo (Figure 1). It reacts with both oxidants with a very high reaction rate constant of more than 10^7 L/(mol-sec). Such a value, in the case of ozone, and especially in the reactions of chlorine dioxide, falls into the class of the highest known reaction rate constants (1,6). There is hardly a contaminant of the reagent solution imaginable, which ozone or chlorine dioxide devour at a comparable reaction rate, and thus compete with the color removal reaction.
7. The oxidation products formed react further with ozone and chlorine dioxide very slowly at best (2,5). This means that a localized temporary excess, which can occur with each addition of ozone, does not lead to a blank demand for the oxidant. However, in the case of the determination of ozone, organic compounds of a type such as the indigo reaction products function as carriers of a radical chain reaction, which might cause a catalytic decomposition of ozone (7). In order to avoid such a chain reaction, the pH of the solution for the determination of ozone is maintained low (pH < 3). In the case of chlorine

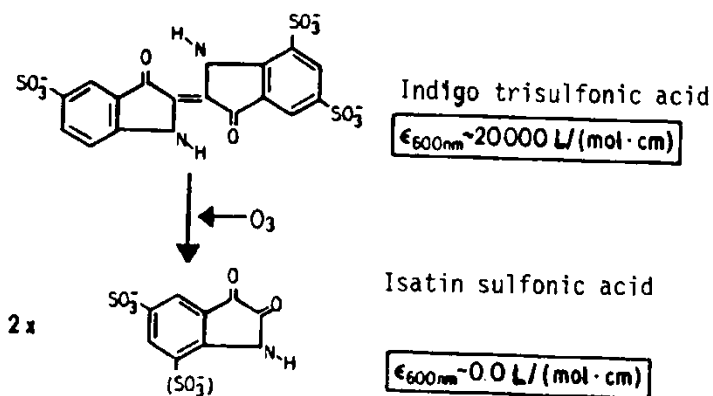


Figure 1. Indigo trisulfonate and its oxidation products.

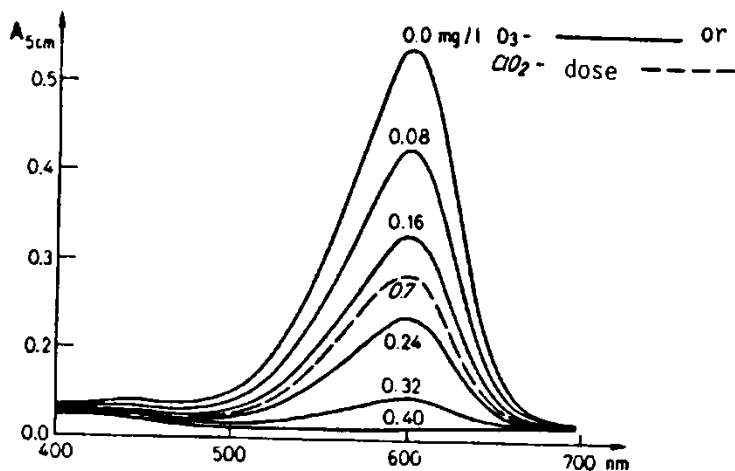


Figure 2. Absorption spectrum of the indigo reagent after different doses of ozone (—) or chlorine dioxide (---). Initial concentration of indigo trisulfonate in final dilution = 10 $\mu\text{mol/L}$.

dioxide, initially produced chlorite ion again produces chlorine dioxide through a slow reaction (6), and interferes with the analysis via this reaction. The determination of chlorine dioxide therefore is carried out at a higher pH (pH > 4).