CHAPTER III

INDICATORS FOR ARGENTOMETRIC TITRATIONS.
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After giving a review of compounds reported in the literature as indicators for argentometric titrations, experimental data on three new argentometric indicators are given.
INDICATORS FOR ARGENTOMETRIC TITRATIONS

Argentometric titrations are widely used for the estimation of halides, sulfur compounds, ferrocyanides etc. Since the description of classical Mohr method in 1860, many substances have been reported as indications for argentometric titrations, and this Section is a review of the literature upto 1970. Most of the indicators suggested are dyes which act as adsorption indicators. They are not particularly sensitive for silver ion, but are adsorbed by the silver halide and undergo a particularly characteristic colour change during the adsorption process. A substance can be used as an indicator only if it is appreciably adsorbed in the immediate vicinity of the end point. As dyes sensitise silver halides, titrations must be carried out rapidly in diffuse light.

A. Azo Dyes as Indicators in Argentometry

Tartrazine gives a yellow colour to AgCl or AgBr which becomes greenish yellow in the presence of a slight excess of chloride or bromide, the colour change being very sharp. It is reported to be more suitable than
p-ethoxychrysoidine may be used for the titration of iodides or thiocyanates with silver nitrate in neutral solution. On addition of the alcoholic solution of the indicator, iodide or thiocyanate solution becomes yellow. On addition of silver nitrate, it becomes rose red, but at the end point it turns pale yellow\(^2\). Congored has properties of acidic dyestuffs like phthaleins as well as those of basic dyestuffs like rhodamines. Hence, it can be adsorbed by positively as well as negatively charged particles giving rise to different colours. It is recommended as an indicator for titration of halides and thiocyanates in the pH range 3-5, the colour change being blue to red\(^4\). A procedure for the determination of iodide in presence of chloride, using congored indicator has also been described\(^5\).

Another substance related to congored in structure is phenyl-1 napthylamine-azobenzene-p sulfonic acid. Between the pH range 3-5, the precipitates of silver chloride or bromide coagulate and adsorb the dye with development of blue colour on the particles. At the equivalent point, the blue colour turns red. The reversibility and sharpness are increased by the addition of chloride free destrin\(^6\).
For titrations of chloride with silver nitrate, acid violet 4BL has been reported to be a good adsorption indicator, the end point being blue-green to violet. Multivalent cations, and anions yielding slightly soluble silver salts do not interfere. It can be used with solutions containing very low chloride concentrations, i.e. 0.001% chloride.

Bordeaux red and Orange II are useful indicators for argentometric determination of halides and thiocyanates. As these dyes are preferentially adsorbed on silver iodide over silver chloride, they can be used for simultaneous determination of chloride and iodide. On titrating the chloride-iodide mixture with silver nitrate in presence of these indicators, a yellow orange end point measures silver iodide and by further titration a second, deep rose end point measures silver chloride.

Brilliant yellow has been suggested as an indicator in titrations of chlorides, bromides and iodides with silver nitrate. The solution should be neutral in case of iodides but 1N nitric acid can be tolerated in case of chlorides and bromides. The end points are red in neutral medium and orange in acidic media.

At pH values higher than 2, brilliant yellow acts as an adsorption indicator for argentometric titrations of bromide, iodide and thiocyanate. If an equal volume of
ethyl alcohol is added, chlorides can also be titrated at pH.210A.

By titrating halides, cyanides, thiocyanates with silver nitrate in presence of varifamine blue, excess silver nitrate can be determined11A. It can also be used as an indicator for the argentometric determination of potassium and nitrogenous organic bases with sodium tetraphenyl boron12A, for the determination of ammonia, ammonium ions and nitrogenous organic ions with potassium tetraphenyl boron13A, and the determination of nitrates and nitro compounds with ammonium tetraphenyl boron14A.

When adsorbed on silver halide precipitate, 4-(2-ethyl-1 phenyl azo)-1 napthylamine hydrochloride behaves like acid. It is a reliable indicator for titrating Ag⁺ with thiocyanate. In the presence of indicator, silver solution is lilac blue. On addition of SCN⁻, it becomes yellow, and at the equivalence point, on the addition of 1 drop of SCN⁻ it becomes lilac again. If the Ag⁺ is titrated with SCN⁻, the optimum pH is 2.8-3.3 (gain of a proton) but if SCN⁻ is titrated with Ag⁺, optimum pH range is 3.5-4.5 (loss of proton). With Br⁻ or I⁻ the final end point is red15A.

Between pH 3.2 and 4.4, p-ethoxy α napthyl red shows sharp multi stage colour changes and has been recommended as an adsorption indicator for argentometric titrations of bromide, iodide, cyanide, sulfocyanide16A.
p-amino azobenzidine, chrysoidine, chrysoidine-R, and Bismark brown has been investigated as indicators for argentometric titrations and p-aminoazobenzene gives excellent end points with iodide or thiocyanate. The end points of chrysoidine and p-ethoxy chrysoidine are quite similar, but the latter is less sensitive. Bismark brown was found to be unsuitable for such titration. For p-amino azobenzene, the optimum pH for titration is 3-4, the colour change at the end point being from golden yellow to pink red. The order of sensitivity is $I^- > CNS^- > Br^- > Cl^-$ whereas for chrysoidine, the optimum pH range is 3.5-5, and the colour change is orange yellow to orange red. The order of sensitivity is $I^- > Br^- > CNS^- > Cl^-$. 17A.

4-(2 ethylphenyl azo)-1-napthylamine hydrochloride has been recommended for bromides and iodides but is unsuitable for chlorides and thiocyanates. 18A.

Trypan blue 19A has also been suggested as a suitable indicator.

4-(4-nitrophenyl azo)-1-naphthol 20A,21A and 2-(4-nitrophenyl azo)-1 naphthol 4 sulfonic acid 22A,23A have been suggested as indicator for chlorides, bromides, thiocyanates and cyanides.
B. Phthalein Dyes

Eosin has been evaluated as an indicator for titrations of Cl\(^-\), Br\(^-\), I\(^-\), CN\(^-\) by silver nitrate. For the titration of chloride ions, the pH should be between 0.5 and 2.0.\(^{1B,2B,21B}\) A 1% solution of eosin in acetic acid (containing 50% ethyl alcohol or acetone) has been suggested, but in the presence of dioxane, a neutral solution can be used.\(^{3B}\) Careful control of acidity is needed during the use of eosin.\(^{1B}\)

Fluorescein and bromophenol blue have been recommended for the determination of Parkopan, Spasman and Dispasmol.\(^{4B}\)

Dichloro-fluorescein is a suitable indicator between pH 3.5 and 4.0.\(^{5B}\) and N-methyl diphenylamine red can be used with 1M nitric acid or 1M sulfuric acid in argentometric titrations.\(^{5B}\)

In titrations of NaCl or KCl with silver nitrate with dichlorofluorescein as indicator, a more accurate and clear cut end point is obtained by observing the character of the precipitate.\(^{6B}\)

Resorcinol-succinein is useful as an indicator in neutral or just alkaline medium but fails in acidic media.\(^{7B}\) The end point is quite sharp and is reversible in dilute solutions.\(^{8B}\) Chloride does not give sharp end point in dilutions greater than 0.02N and bromides do not give sharp end point in dilutions greater than 0.005N.\(^{9B}\)
Dibromoresorcinol succinic acid is unsuitable for chloride determination in neutral or acidic solutions but a sharp end point is obtained with bromide, thiocyanate or iodide in acid solution.\(^\text{(10B)}\)

Tetrabromoresorcinol succinic acid can be used for titrations of bromide, iodide and sulfocyanide in neutral or acidic media.\(^\text{(10B)}\)

Resorcinol maleic acid, resorcinol itaconic acid, resorcinol citraconic acid, resorcinol acetic acid are unsuitable as indicators for argentometric titrations, but resorcinol tricarballyl gives sharp end points in the titrations.

Resorcinol quinoline and Resorcinolcinchonidine are suitable indicators for thiocyanate, bromides and iodides, but these substances cannot be used for bromide in ammonical solutions or at pH values beyond 6. With iodides, the end point is obtained even at as low a concentration as 0.001N iodide.\(^\text{(12B)}\)

Tetrabromoresorcinol quinoline and tetrabromoresorcinol-cinchomerine have also been suggested for iodide. In neutral medium the end point is the disappearance of pink colour whereas in acidic or ammonical solution, the suspension changes from yellow to pink.\(^\text{(12B)}\)

Dyes prepared from the condensation of resorcinol with 4, 5 dihydrophthalic acid, 1, 4, 5, 6 tetrahydrophthalic acid, phenyl succinic acid, o-chlorophenyl
succinic acid$^{14B}$ and methyl succinic acid$^{14B}$ are as good
as fluorescein in argentometric titrations. The dyes
prepared by the condensation of resorcinol with tetra-
phenyolphthalic acid$^{13B}$, 3,4,5,6 tetraphenyl, 1-2 dihydro-
phthalic acid$^{13B}$, 1,2 dihydrophthalic acid$^{13B}$, 3,6 diphenyl
1,2,3,6 tetrahydrophthalic acid$^{13B}$, o-nitrophenyl succinic
acid$^{14B}$, p-nitrophenylsuccinic acid$^{13B}$, phenylsuccinic
acid$^{14B}$, as well as those prepared by condensation of
phloroglucinol, catechol, pyrogallol or orcinol with
1,4,5,6 tetra hydrophthalic acid$^{14B}$ are not suitable.

Tetraresorcinol pyromellitenein and diresorcinol diphenol
pyromellitenein have been used as argentometric indicators
for halides and thiocyanate. Diresorcinol diphenol
pyromellitenein is an excellent indicator which can be used
even in the presence of coloured ions like Cr$^{3+}$, Fe$^{3+}$,
Cu$^{2+}$, Ni$^{2+}$ and Co$^{2+}$$^{15B}$.

N-N bis (Carboxy methyl) aminomethyl fluorescein can be
used as indicator for iodide and bromide at pH 9, but for
the determination of cyanide, pH should be maintained at
11$^{16B}$.

At pH 7, 0.02N chloride, 0.005N bromide or thiocyanate or
0.001N iodide can be titrated with catechol violet indicator,
the colour change near equivalent point being yellow
to blue for chloride and thiocyanate and yellow to green
for bromide and iodide$^{17B}$.

In the pH range 4-7, ammonium salt of pyrogallol red has
been suggested. At the equivalent point, the pink suspension becomes blue with chloride and green in case of bromide or iodide. In this way, 0.01N chloride, 0.002N bromide, 0.005N iodide and 0.002N sulfocyanide can be successfully titrated.\(^7\)

The ammonium salt of phthalein complexone is added to the halide solution and 0.1N sodium hydroxide or ammonium hydroxide is added dropwise till the mixture becomes pink. It is then titrated with silver nitrate till the precipitate turns blue (chloride or sulfocyanide) or green (bromide or iodide). The limits are 0.01N chloride, 0.002N bromide or thiocyanate and 0.0005N iodide.\(^7\)

In the presence of xylenol orange, the halides are pink in alkaline medium. At the end point, the pink suspension changes to a greyblue precipitate for thiocyanate and to a grey green precipitate for bromide or iodide. The limiting concentrations are 0.01N thiocyanate, 0.005N bromide, or 0.001N iodide.\(^7\)

Calcein is an efficient indicator provided the pH is maintained between 2.5 and 8.5, the end point being yellow suspension to pink precipitate; 0.01N thiocyanate, 0.002N bromide or 0.0005N iodide can be thus titrated.\(^7\)

At pH 7, the halide solution is flesh coloured in presence of murexide but turn violet at the end point; 0.02N chloride, 0.01N thiocyanate, 0.002N bromide or 0.001N iodide can be titrated with this indicator.\(^7\)
Unsymmetrical phthaleins prepared by the condensation of resorcinol or orcinol with 2-acetyl-3,4,5,6 tetrachlorobenzoic anhydride are reported to be satisfactory for titrations of silver nitrate, with chloride, bromide or iodides. The resorcinol derivative is more efficient, and in the presence of dextrin, the colour change is more vivid.

Iodofluorescein, phloxine, and erythrosine have also been suggested. Iodophenol blue gives a red yellow to grey green end point for iodide; red yellow to sky blue end point for bromide and rose yellow to rose violet for chloride.

Mixtures of (1) rhodamine 6G and methylene blue (2) rhodamine 6G and fluorescein and (3) methylene blue and fluorescein have been suggested as indicators for titration of AgNO₃ with Br⁻. The first two mixtures are suitable in pH range 1.34 to 7.0 whereas the third is suitable in pH range 6 to 9.4.

C. Azine Dyes

Neutral red has been suggested as an indicator for argentometric titrations of iodides and bromides. The titration can be carried out in a highly acid medium.

1, 2-benzo 3-amino, 7-phenoxazine has been reported as a fluorescence indicator for determinations of halides by argentometry. More complex azines have been used as indicators for argentometric titrations of neutral solu-
tions of chlorides, bromides and iodides. The colour
change is from a yellow suspension to a pink precipitate.
0.005M-0.05M halides can be titrated but the optimum
halide concentration is 0.01M3C4C.

1-2 benzo-3(1 napthylamino),7 dimethyl aminophenoxazi-
nium chloride has been reported as a suitable argento-
metric indicator2C.

D. Diphenyl Methane Dyes

Bromophenol blue has been suggested as an indicator for
the argentometric titration of thiocyanate1D and
between pH 2.7 and 3.4 is a satisfactory adsorption
indicator for the argentometric determination of chloride
in Soy Sauce and Miso2D. The results are accurate in
the presence of considerable amounts of proteins, amino
acids, and other organic compounds. Under the same con-
dition, metanil yellow, tropeolin 00, fluorescein,
dichlorofluorescein, congo red, etc. cannot be used owing
to the interference of protein and its hydrolysate or
fermented products2D. Volhard's and Mohr's methods are
also unsatisfactory2D.

Between pH 8 and 10 phenolphthalein is adsorbed appreciably
by AgCl-Ag⁺ systems and can be used as an indicator for the
argentometric titration of chloride, the end point being
marked by an appearance of pink precipitate3D.

Aniline blue can be used as an indicator for the argento-
metric titration of iodide, the limiting concentration
being 0.02N. The suspension becomes greenish-blue at
the end point.\textsuperscript{4D}

Alkali blue is useful in the pH range 2.1-9.3 where
chloride and iodide can be simultaneously determined.
Firstly, iodide can be titrated to the transition of
violet blue into green blue, then the precipitation of
chloride is finished. The titration of iodide should
be carried out in artificial light.\textsuperscript{4D}

Eriogreen B has been reported to be a satisfactory
indicator for the argentometric titrations of bromide,
iodide or sulfocyanide\textsuperscript{5D}, while chlorophenol blue has
been studied as an adsorption indicator for the argento-
metric titration of 0.02 N chloride, bromide and iodide\textsuperscript{6D}.
Between pH 3.0 and 4.0 chlorobromophenol blue is success-
ful as an argentometric indicator for halides, the limit-
ing concentrations being 0.02 N Cl\textsuperscript{-}, 0.01 N Br\textsuperscript{-} and
0.01 N I\textsuperscript{-}\textsuperscript{6D}, whereas phenol red, cresol red, thymol
blue, bromophenol red, bromocresol purple, chlorophenol
red, iodophenol blue, chlorophenol blue and chlorobromo-
phenol blue are unsuitable in Soy Sauce and Miso. Tetra-
bromophenol blue\textsuperscript{6D} can be used, and Fuschin has also been
suggested\textsuperscript{19A}.

\textsuperscript{7D}Bromopyrogallol red and o-phenanthroline give a red
sharp well defined end point in the concentration range
10\textsuperscript{-1} to 10\textsuperscript{-4} M.\textsuperscript{7D}

Bromochlorophenol blue, bromophenol red, o-cresol red
and m-cresol purple, have been investigated as indicators for argentometric titrations. Reported results are that bromochlorophenol blue is useful for chloride, bromide, iodide and thiocyanate determinations, bromophenol red for the determination bromide, iodide, and thiocyanate, whereas o-cresol red and m-cresol purple are suitable for iodide and thiocyanate determinations.

Erischrome black has also been reported as an indicator.

E. Other Dyes

The addition of orthochrome-T to a chloride solution colours it red, but if silver nitrate is added, the dye is adsorbed over the precipitate, turning it lilac, and the solution becomes colourless. At the end point, the dye is desorbed, leaving a white precipitate and a reddish solution. 1,5 dianilinopentamethine chloride is a suitable adsorption indicator for argentometric determinations, the end point being yellow.

Martius yellow gives a brick red colour at the end point in the titration of halides, the limiting concentration being 0.0002 N. Xylenol orange is a satisfactory indicator.

F. Amines

The sulphates of 3-methyl benzidine and 3-3 diethyl benzidine are reported to be more effective indicators for the argentometric titrations of bromide and iodide.
than benzidine sulphate. The colour change is yellow to blue green. Ferric (ceric or vanadate) complexes of o-tolidine are satisfactory indicators. 

The ferric complexes of benzidine, toldidine, and o-dianisidine are suggested as adsorption indicators for the argentometric titrations of chloride, the end-point being blue or violet.

For the titration of 0.001, 0.01, and 0.1 N silver nitrate with thiocyanate, Cu++-benzidine, in weakly citric acid solution, can be used as an indicator, and the determination carried out in the presence of Pb++ and Cu++. Cu++-o anisidine is a good indicator for determination of Ag+ with chloride, bromide or iodide in citric acid or in dilute nitric acid. Cu++-toluidine in citric acid is a satisfactory indicator for silver in the presence of Cu+++, Cr++, Co++, and Ni++. Ferric-benzidine, ferric-o-dianisidine, and ferric-toluidine complexes are excellent indicators for the argentometric titrations of chloride in acid solutions, where 10% concentrated nitric acid can be tolerated. These substances are also reported to be satisfactory indicators for titrations of bromides in acid media, the amounts of nitric acid tolerated by 0.1, 0.01, and 0.001 N Br⁻ are 30%, 15%, and 8% respectively.
In the presence of nitric acid, vanadate-o-toluidine, vanadate-o-dianisidine and vanadate-benzidine act as argentometric indicators. Chlorides, bromides, iodides and thiocyanates can be titrated in this manner.

Auric-o-dianisidine is used as an indicator in titrations of iodides with silver nitrate, and 5.5 N nitric acid can be tolerated by the system.

For the simultaneous titration of iodide and bromide mixtures, the ferric-benzidine system has been utilized.

Vanadate-tetra methylaminodiphenylmethane and Mo++ diphenyl carbazide have been suggested as indicators for argentometric titrations of iodides and chlorides in the presence of each other.

In the argentometric determination of bromides, ferrous phenanthroline tolerates high concentration of acids (about 28.5 N H3PO4).

For argentometric titrations of chlorides, bromides, iodides, and thiocyanates, in the presence of vanadates, or ferric ions, di-o-phenetidine has been suggested as an indicator. Naphthidine can also be used for iodides.

In the presence of iodine, tetrabase has been used as an indicator for titration of chlorides. In the presence of vanadates, it is useful as an indicator for the titration of chlorides or bromides.
In the presence of \( \text{Hg}^{++} \) ions diphenylthiocarbazide is recommended as an indicator for chlorides, bromides, and thiocyanates\(^8\).

Erioglaucine, in the presence of \( \text{Ce}^{++++} \), is reported as suitable for titrations of bromides and iodides\(^8\).

With \( \text{Ce}^{++++} \) Lissamine can be used for titration of iodides and thiocyanates\(^8\).

Septopalmine in presence of \( \text{MnO}_4^- \) is reported as suitable for iodides but for thiocyanates \( \text{Ce}^{++++} \) should be added\(^8\).

Diphenylamine, N-methyldiphenyl-amine red, benzidine, o-dianisidine and o-tolidine are suitable for the determination of chloride in Soy Sauce and Miso, the best results being given by benzidine and o-tolidine in presence of ferric ions\(^1\).

Diphenylamine and potassium metavanadate have been used as indicator for titration iodide in presence of \( \text{Br}^- \) or \( \text{Cl}^- \)\(^6\).

Where ceric ammonium sulfate \( o-o' \) is present, di-isopro-poxybenzidine can be used\(^7\).

For the titrations of chlorides, bromides and iodides, 3-3'-dimethyl naphthidine has been used. At the end point, the solution turns red\(^8\).

2-5 bis(2 hydroxy-ethylamino) terephthalic acid is reported to be a very sensitive indicator for argentometric
titrations and chlorides of bismuth and other trivalent metals can be titrated argentometrically using this indicator, as can iodides, sulphides and thiocyanates. In the titrations of iodides, the temperature should be maintained at 90°C or, alternatively, 0.1 N sodium acetate should be added and the titration be carried out at room temperature. In the titration of sulphides, potassium nitrate should be added to suppress the loss of H₂S.

G. Miscellaneous

Diphenylcarbazone is suitable for titrations of halides, the colour change being from red to violet with chlorides, from red to yellow or yellow-green with bromides or iodides, and from red to blue with thiocyanates.

Mercury-diphenylacarbazide has also been studied, the end-points being violet for chloride and bromides, blue for thiocyanates and green for iodides. The titration should be carried out in diffuse light.

P-dimethylaminobenzylidene-rhodanine has been recommended as an internal indicator for the titrations of chlorides and bromides with silver nitrate. The presence of 6 N nitric acid or 10 N sulphuric acid can be tolerated.

It has been used as indicator for titration of silver nitrate with potassium ferrocyanide, potassium thiocyanate, potassium iodide, sodium tetraphenylboron, thiourea, thiosemicarbazide, thioacetamide, o-phenylene thiourea, diphenylthiourea, methylmercaptan, isoamylmercaptan, β-naphthylmethylmercaptan, mercapto-propionic acid and thiophenol; the
colour change being from yellow to red or purple. Sulphates, phosphates, nitrates, fluorides, sulphites, EDTA, thallium I, lead II, Fe II, Fe III, Cu II do not interfere in these titrations 4G.

Pyramidone has been reported to be an excellent argentometric indicator, at its most sensitive in the pH range 4.5-9.6, the end point being blue. It can be used to determine chlorides, bromides, iodides and thiocyanates argentometrically 5G. Potassium rhodizonate has also been proved suitable, but it cannot be used in acid solutions 6G.

3,7,5',6' tetrahydroxy-3,4 dihydroindene (2',1':3,4) cumine is used as an adsorption indicator for argentometric titrations of bromides, iodides and thiocyanates 7G. The colour changes near the end point are as follows:

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<thead>
<tr>
<th></th>
<th>Br⁻</th>
<th>I⁻</th>
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<tbody>
<tr>
<td>Acid medium</td>
<td>Yellow to pink</td>
<td>Yellow to pale blue</td>
</tr>
<tr>
<td>Neutral medium</td>
<td>Red yellow to azure</td>
<td>Red yellow to green blue</td>
</tr>
<tr>
<td>Alkaline medium</td>
<td>Red to azure</td>
<td>Red to azure</td>
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Bixin, extracted from Bixa orellana, functions as an argentometric indicator, the end-point being marked by a rose precipitate.

In the titration of silver nitrate with iodides, Dithizone can be used, the colour being green at the end-point 8G.
During titrations of chlorides with silver nitrate with 2,6 dichlorophenolindophenol indicator, the precipitate becomes pink at the end point, while with bromides the precipitate is yellow-buff, the supernatant liquid being bluish-violet in both the cases. The solutions must be neutral. The indicator is not suitable for titration of iodides as the colour change is not sharp.

Lucigenin is reported to be a suitable adsorption indicator for iodide in the presence of chlorides and bromides, but cyanides and thiocyanates interfere. At the end-point, lucigenin is desorbed from silver iodide and the solution luminesces. 2-aminobenzimidazole has also been used.

1 phenyl, 1 hydroxy 3 methyl thiourea has been suggested as an indicator for direct and reverse argentometric titrations of chloride, bromide, iodide and thiocyanate. The colour change at the end point is white to deep pink for direct titration and pink to yellow for reverse titration and occurs only in the presence of sodium acetate. PO$_4^{3-}$, SO$_3^{2-}$, S$_2^{2-}$, F$^-$, S$_2$O$_3^{2-}$, Fe(CN)$_6^{4-}$, CrO$_4^{2-}$, CO$_3^{2-}$, interfere strongly. VO$_2^+$, Th$^{4+}$, Cu$^{2+}$, Sc$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Pd$^{2+}$, Pt$^{4+}$, Mo$^{6+}$, W$^{5+}$ also interfere seriously.
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E. Popper, L. Roman, Eleonora Tabara and M., Serban, 

B. **PHTHALEIN DYES**

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18B. Unsymmetrical phthaleins of 2-acetyl, 3,4,5,6-tetra-chlorobenzoic acid as indicators.
S.P. Mushran, P. Sanyal, S.K. Gandhi,

19B. Phenolsulfonaphthalein derivatives as adsorption indicators for argentometry,
G. Aliotta and A.R. Casal,

20B. Mixed adsorption indicators in argentometry.
I.N. Bulanzhe, G.A. Mel'nik,

21B. New indicators in argentometry,
O. Tomicek,
Casopis Ceskolovenskeho Lekarnictva, 5 C 1-3, 15-6,
as per C.A., 21, 3848 (1927).

C. AZINE DYSES

1C. Iodine-neutral red systems as adsorption indicators,
F. Sierra, G.A. Mora,
Anales real soc. espan. fis y quim (Madrid),


D. DIPHENYL METHANE DYES


E. OTHER DYES


1F. Argentometric determination by the use of Fe$^{3+}$ (Ce$^{4+}$
or VO$^{3-}$)-o-tolidine system as an oxyadsorption indicator.
K. Sato,

2F. New argentometric determination of chlorides, with meriquononoid derivatives of benzidine, tolinine,
and o-dianisidine as adsorption indicators.
F. Sierra, J.H. Canavate,
Anales real soc. espan. fis. y. quim. (Madrid),
47B, 439 (1951), as per C.A. 46, 379 (1952).

3F. New argentometric determinations with adsorption indicators.
J.H. Canavate,
Anales. univ. Murcia, 10, 275 (1951), as per C.A. 47, 5301 (1953).

4F. New argentometric determinations of mixtures of halides with adsorption indicators.
F.R.R. Sandez,

5F. New indicators for oxy-adsorption,
G.S. Essen,
Anales Univ. Murcia, 16 (1957), C151 as per C.A. 54 5324 (1960).

6F. New applications of the diphenyl amine indicator in volumetric oxygen-adsorption reaction.
F. Sierra, G. Amensi,
A.A. 8, 4248 (1959).

7F. Alkoxybenzidine derivatives as adsorption indicators for oxidation reduction titrations.
F.S. Jimenez, A.A. Martinez, F.C. Cebrain,

8F. Argentometric determination of chloride, bromide and iodide in the presence of 3,3'-dimethylnaphthidine,
Z. Gregorowcz, S. Kovalski,
9F. 2,5-Bis(2-hydroxyethylamino) terephthalic acid as an indicator in argentometry.
E. Uhlig,

10F. 2,5-Bis(2-hydroxyethylamine) terephthalic acid as an indicator in argentometry II.
E. Uhlig, K. Richter,

G. MISCELLANEOUS

1G. New indicators for argentometric titrations.
E. Chirnoaga,

2G. The indicator system Hg\(^{++}\) -diphenyl carbazide.
F. Sierra, C.S. Pedreno,

3G. Argentometric titration with p-dimethylaminobenzylidenenrhodanine as an internal indicator.
H. Goto, S. Sato,

4G. Mercurimetric and Argentometric titrations using p-dimethylamine benzyl-imidennerhodanine as indicator.
M. Wronski,
Talanta, 12, 593 (1965).

5G. Use of pyramidone as indicator in argentometry,
G.A. Vaisman,
Aptechnoe Delo., 1952, 30, as per C.A., 46, 6989 (1952).

6G. Potassium rhodizonate as an indicator in argentometric titrations.
J.P. Mehlig,
Chemist Analyst, 44, 87 (1955), as per C.A. 50, 1517 (1956).

7G. Adsorption indicators, VI.
G. Mannelli, P. Nancini,


EXPERIMENTAL:
The colour reactions of silver ions with gentisaldehyde, gentisaldoxime and sodium gentisate have been employed to detect end points of argentometric titrations.

The effect of variables such as silver nitrate concentration, indicator concentration, pH, temperature and foreign ions have been investigated.

Materials:

(1) Silver nitrate solution:
A stock solution of silver nitrate (0.1M) was prepared by dissolving 16.99 gms. silver nitrate in distilled water and making upto 1 liter.

(2) Halide solutions:
A stock solution of 0.1M sodium chloride, sodium bromide or potassium iodide was prepared by dissolving requisite amount of the analar salt in distilled water.

(3) Indicator solutions:
1% solutions of the gentisaldehyde and gentisaldoxime were prepared from pure samples of the reagents by dissolving the requisite amount of the compound in 95% alcohol. 1% solution of sodium gentisate was prepared in distilled water. The solutions were stable upto 1 week.
(4) Metal solutions:
To study the interferences of various foreign ions in the estimation of halides by argentometric titration, the corresponding analar quality of salts were taken and their 0.2M solutions prepared in distilled water. With the indicators, the titrations can be carried out with silver nitrate in burette, the colour change at the end point being colourless to grey. During the titration, the solution remains clear, but becomes viscous and as the end point approaches, the silver halide separates as a precipitate; after the addition of one more drop of silver nitrate, the solution appears grey.

Effect of pH:
The effect of pH on accuracy of titration with these indicators in shown in Fig. III-1. Accurate results are obtained in the pH range 5.5-6.5. Outside this range, the accuracy of titration decreases.

Effect of indicator concentration:
Titrations were carried out with different proportions of the indicator, and it was found that an addition of 3 drops of 1% indicator solution in ethanol to 5 ml of titre solution gives accurate and sharp end point.

Effect of silver nitrate concentration:
0.1M, 0.05M, 0.001M solutions of silver nitrate were titrated with halide solutions using the suggested
indicators. The results are given in Table No. III-1, p. 96. With these indicators, the lowest concentration titrable is 5 ml. of 0.001M halide.

**Effect of temperature:**

The titration could be satisfactorily carried out in the temperature range 5°-60°C. (Table III-2, page 99)

**Effect of foreign ions:**

Preliminary investigations indicated that $PO_4^{3-}$, $AsO_4^{2-}$, $SO_3^{2-}$, $S^{2-}$, $F^-$, $S_2O_3^{2-}$, $Fe(CN)_6^{4-}$, $CNS^-$, $CrO_4^{2-}$, $CO_3^{2-}$, $Mo^{6+}$, $W^{6+}$ interfere seriously. It was observed that at 17.7 mg concentration of chloride (or 40 mg concentration of bromide ions or 63.45 mg concentration of iodide) 23 mg. Na⁺, 39 mg K⁺, 18 mg NH₄⁺, 65.3 mg Cu²⁺, 24.3 mg Mg²⁺, 23.6 mg Ca²⁺, 137.3 mg Ba²⁺, 65.3 mg Zn²⁺, 112.4 mg. Cd²⁺, 27 mg Al³⁺, 54.9 mg Mn²⁺, 55.8 mg Fe²⁺, 59.0 mg Co²⁺, 58.6 mg. Ni²⁺ and 96 mg $SO_4^{2-}$ could be tolerated (Table III-3).

**Applications:**

The indicators have been used for determining total halides in water (Table III-4, page 101) and to ascertain percentage purity of a sample of potassium bromide and potassium iodide (Table III-5, page 103).

**Conclusions:**

Gentisaldehyde, Gentisaldoxime and sodium gentisate are satisfactory indicators for argentometric titrations. They probably act by reducing the excess silver nitrate to metallic silver which is absorbed on the silver halide precipitate.
Fig. III-1. Effect of pH on accuracy of titration.
<table>
<thead>
<tr>
<th>Concentration of Halide</th>
<th>0.1M</th>
<th>0.05M</th>
<th>0.01M</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNO₃ Concentration</td>
<td>0.1M</td>
<td>0.05M</td>
<td>0.01M</td>
</tr>
<tr>
<td>Titre values of AgNO₃ in ml.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Chloride:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Gentisaldehyde</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>(ii) Gentisaldoxime</td>
<td>5.00</td>
<td>5.01</td>
<td>5.00</td>
</tr>
<tr>
<td>(iii) Sodium gentisate</td>
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<td>5.00</td>
<td>5.00</td>
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<tr>
<td>B. Bromide:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Gentisaldehyde</td>
<td>5.00</td>
<td>5.00</td>
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<tr>
<td>(iii) Sodium gentisate</td>
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<tr>
<td>C. Iodide:</td>
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<tr>
<td>(i) Gentisaldehyde</td>
<td>5.00</td>
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<td>(iii) Sodium gentisate</td>
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<tr>
<td>Temperature</td>
<td>0-5°C</td>
<td>35°C</td>
<td>50-60°C</td>
</tr>
<tr>
<td>-------------</td>
<td>-------</td>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>Indicator</td>
<td>Titre values of AgNO₃ in ml.</td>
<td></td>
<td></td>
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<tr>
<td>A. Chloride:</td>
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<tr>
<td>(i) Gentisaldehyde</td>
<td>5.00</td>
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<td>(ii) Gentisaldoxime</td>
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<td>B. Bromide:</td>
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<td>C. Iodide:</td>
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<td>(i) Gentisaldehyde</td>
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TABLE III-3
EFFECT OF FOREIGN IONS ON THE ACCURACY OF TITRATION

<table>
<thead>
<tr>
<th>Interfering Ion (and its concentration)</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>NH₄⁺</th>
<th>Cu²⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Sr²⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(23 mg)</td>
<td>(39 mg)</td>
<td>(18 mg)</td>
<td>(63.5 mg)</td>
<td>(24.3 mg)</td>
<td>(23.6 mg)</td>
<td>(283 mg)</td>
<td>(137.3 mg)</td>
</tr>
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<td>A. Chloride:</td>
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<tr>
<td>(i) Gentisaldehyde</td>
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<tr>
<td>(ii) Gentisadoxime</td>
<td>5.00</td>
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<tr>
<td>(iii) Sodium gentisate</td>
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<td>B. Bromide:</td>
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<td>(ii) Gentisadoxime</td>
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<td>(iii) Sodium gentisate</td>
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<tr>
<td>C. Iodide:</td>
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<tr>
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</tbody>
</table>

pH of Titration: 5.5
Concentration of halide ion: 0.1M
Concentration of AgNO₃: 0.1M
Titre volume: 5 ml.
<table>
<thead>
<tr>
<th>Interfering Ion (and its concentration)</th>
<th>Zn$^{2+}$ (65.3 mg)</th>
<th>Cd$^{2+}$ (112.4 mg)</th>
<th>Al$^{3+}$ (27 mg)</th>
<th>Mn$^{2+}$ (54.9 mg)</th>
<th>Fe$^{2+}$ (55.8 mg)</th>
<th>Co$^{2+}$ (59.0 mg)</th>
<th>Ni$^{2+}$ (58.6 mg)</th>
<th>SO$_4^{2-}$ (96 mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Chloride:</td>
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<td>B. Bromide:</td>
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<td>C. Iodide:</td>
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<tr>
<td>(i) Gentisaldehyde</td>
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<td>5.00</td>
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<tr>
<td>(ii) Gentisaldoxime</td>
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</tbody>
</table>
TABLE III-4
APPLICATION OF THE INDICATORS TO THE DETERMINATION OF TOTAL HALIDES IN WATER

Several samples of water were collected and analysed for total halides by argentometric titration with the help of the suggested indicators.

Concentration of AgNO₃ : 0.1M  
Titre volume of water : 25 ml.  
P H of titration : 5.5

<table>
<thead>
<tr>
<th></th>
<th>K₂CrO₄</th>
<th>Gentisaldehyde</th>
<th>Gentisaldoxime</th>
<th>Sodium gentisate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Titre</td>
<td>Halide, p.p.m.</td>
<td>Titre</td>
<td>Halide, p.p.m.</td>
</tr>
<tr>
<td></td>
<td>Volume, ml.</td>
<td>(as Cl⁻)</td>
<td>Volume, ml.</td>
<td>(as Cl⁻)</td>
</tr>
<tr>
<td>Sample A</td>
<td>11.4</td>
<td>1619</td>
<td>11.4</td>
<td>1619</td>
</tr>
<tr>
<td>Sample B</td>
<td>10.0</td>
<td>1420</td>
<td>9.9</td>
<td>1409</td>
</tr>
<tr>
<td>Sample C</td>
<td>8.5</td>
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<tr>
<td>Sample D</td>
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<td>Sample F</td>
<td>10.5</td>
<td>1491</td>
<td>10.5</td>
<td>1491</td>
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</table>
3.0 gms. of a commercial sample of potassium bromide was weighed accurately dissolved in distilled water and the solution was made upto 250 ml. Similarly 250 ml. solution was prepared from 3.75 gms. commercial potassium iodide. A 25 ml. aliquot of the solution was titrated with 0.1N silver nitrate using the suggested indicators.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Titre volume (ml)</th>
<th>% Purity of the sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium bromide:</td>
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<td>K$_2$CrO$_4$</td>
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<td>93.25</td>
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<td>Gentisaldehyde</td>
<td>23.5</td>
<td>93.25</td>
</tr>
<tr>
<td>Gentisaldoxime</td>
<td>23.45</td>
<td>93.00</td>
</tr>
<tr>
<td>Sodium gentisate</td>
<td>23.5</td>
<td>93.25</td>
</tr>
<tr>
<td>Potassium iodide:</td>
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<td></td>
</tr>
<tr>
<td>K$_2$CrO$_4$</td>
<td>20.0</td>
<td>88.54</td>
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<td>Gentisaldehyde</td>
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<td>88.54</td>
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<td>Gentisaldoxime</td>
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<td>88.10</td>
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<td>88.54</td>
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