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A COMPARATIVE STUDY OF SOME LANTHANON CHELATES OF ALIZARIN COMPLEXAN AS REAGENTS FOR FLUORIDE

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Summary—A study has been made of the comparative suitability of the cerium^{III}, lanthanum and praseodymium chelates of alizarin complexan as reagents for the spectrophotometric determination of microgram amounts of fluoride. The cerium^{III} reagent is most sensitive at pH $< 4{\cdot}5$ and the lanthanum reagent at pH $\geqslant 5{\cdot}0$. An enhancement of sensitivity may be obtained for both reagents at pH 4·3 by addition of acetone to 25% v/v, but the most sensitive means of determination is to use the lanthanum reagent in aqueous solution at pH 5·2 with measurement at 281 mμ. This procedure is 200% more sensitive than the standard method at 620 mμ.

LEONARD and West[1] have previously observed that fluoride ion forms soluble blue coloured ternary complexes with the red alizarin complexan chelates of the first few elements of the lanthanon series, *viz.* lanthanum, cerium^{III} and praseodymium. The fourth and fifth members of the series, neodymium and promethium, were not available but the ensuing rare earth, samarium, showed only slight colour formation and subsequent members showed no colour formation at all. At pH 4·3, the cerium^{III} reagent was found to be more sensitive than the others.

It has since been suggested[2] that the lanthanum reagent has advantages over the cerium^{III} reagent on the grounds of sensitivity, but comparative data have been lacking. In the present paper comparative studies have been made and a more sensitive procedure has been developed.

TABLE I. DIFFERENCE IN OPTICAL DENSITIES BETWEEN ALIZARIN COMPLEXAN CHELATES AND THEIR TERNARY FLUORIDE COMPLEXES

Wavelength of measurement, mμ	Difference in optical densities × 10^3						
	pH 4·3				pH 5·7		
	Ce	La	Pr	Sm	Ce	La	Pr
590	186	171	147	19	174		35
600	194	172	152	13	174	182	40
610	199	173	161	6	200	207	50
620	188	165	152		204	210	52
630	160	135	128		178	184	42

Reagents based on lanthanum, cerium^{III} and praseodymium were compared at pH 4·3 and 5·7 in sodium acetate buffers under carefully controlled conditions. The results shown in Table 1 were obtained with solutions containing 5×10^{-6} of a mole each of alizarin complexan, the lanthanon nitrate and sodium fluoride in a total volume of 100 ml. The lanthanon solutions were prepared from "Specpure" materials and their stock solutions were standardised against EDTA using Xylenol Orange as indicator at pH 5·1, before dilution. These results indicate clearly that at pH 4·3, when interferences with the method are likely to be less than at higher pH values, the cerium^{III} reagent is slightly superior to those based on lanthanum and praseodymium. In all three cases the maximum sensitivity towards fluoride occurs at 610 mμ. The samarium-based reagent develops only a slight colour with fluoride and the maximum absorption occurs at 590 mμ. A gadolinium based reagent similarly formulated showed no optical activity whatsoever towards fluoride ion under these conditions. At pH 5·7 all three reagents showed maximum sensitivity towards fluoride ion at 620 mμ. It would appear that at this pH the ternary praseodymium complex is partly hydrolysed as there is a marked fall in absorption. There is a slight enhancement for cerium^{III}, but it is considerably more marked with the lanthanum reagent which at this pH is slightly (*ca.* 3%) more sensitive than the cerium^{III} reagent under the same conditions.

Comparison of lanthanum and cerium^{III} reagents over pH range 4·3–5·9

A narrower pH range was studied by preparing calibration curves (5–50 μg) for fluoride ion based on 1:1 lanthanum and cerium^{III} chelates of alizarin complexan. Repeated check experiments revealed that at pH 4·3 (610 mμ) the cerium^{III} reagent was, as reported previously,[1] slightly more sensitive than the reagent based on lanthanum. At pH 4·5 (610 mμ) the difference in sensitivity between the two reagents becomes vanishingly small. At pH 5·1 (620 mμ) the lanthanum based reagent is approximately 4% more sensitive than the cerium^{III} reagent and this slight advantage is maintained at pH 5·5 and pH 5·9. At both of these pH values there is, however, a decrease in sensitivity for lanthanum as well as for cerium^{III}.

Enhancement of sensitivity

It has previously been reported that the ternary complex between cerium^{III}, alizarin complexan and fluoride ion may be extracted from aqueous solution with a non-miscible organic solvent.[1] In this process an enhancement of sensitivity is obtained. The enhancement, apart from the concentration factor, may be caused by the effect of lower dielectric constant favouring association of the complex and replacement of the co-ordinated water molecule still attached to the cerium^{III} ion in the ternary complex.[1] Accordingly, the effect of the addition of miscible solvents was examined because it was expected that a similar enhancement would result.

Four suitable solvents, two alcohols, one ketone and an ether were examined at pH 4·3, all at the same concentration (20% v/v). The results of this examination, shown in Table II, indicate the superiority (under the specified conditions) of acetone with its sterically unhindered keto-oxygen atom, relatively high basicity and low dielectric constant. Despite the basicity of its oxygen atoms, dioxan is nearly as effective as ethanol, presumably because of its lower dielectric constant. Similarly, methanol is less effective than the other solvents.

The cerium^{III} and lanthanum reagents were next compared in a 20% acetone medium and their performance was checked against variation of pH. This series of experiments revealed that acetone had a more pronounced effect on the lanthanum reagent. The optimum sensitivity in a 20% acetone medium was obtained at pH 4·3 and the wavelength of maximum difference shifted from 610 to 620 mμ. Under the

TABLE II. EFFECT OF SOLVENTS ON THE SENSITIVITY OF THE LANTHANUM METHOD
5 × 10^{-6} MOLE OF LANTHANUM CHELATE + 25 μg OF F^-/100 ml.

Wavelength of measurement, mμ	Optical density × 10^3											
	Methanol			Ethanol			Acetone			Dioxan		
	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity	Chelate	Fluoride complex	Sensitivity
600	178	289	111	134	280	146	159	312	153	110	250	140
610	155	274	119	107	265	158	124	301	177	85	244	159
620	123	247	124	77	237	160	91	267	176	60	222	162
630	096	210	114	51	193	142	61	215	154	38	183	145

Table III. Effect of acetone concentration on sensitivity of lanthanum reagent. 5×10^{-6} mole of lanthanum chelate + 25 μg of F^-/100 ml

Acetone, %	Optical densities (at 620 mμ) × 10^3		
	Lanthanum chelate	Fluoride complex	Sensitivity
10	70	220	150
15	92	265	173
20	111	296	177
25	136	316	180
30	153	327	174
35	170	334	164

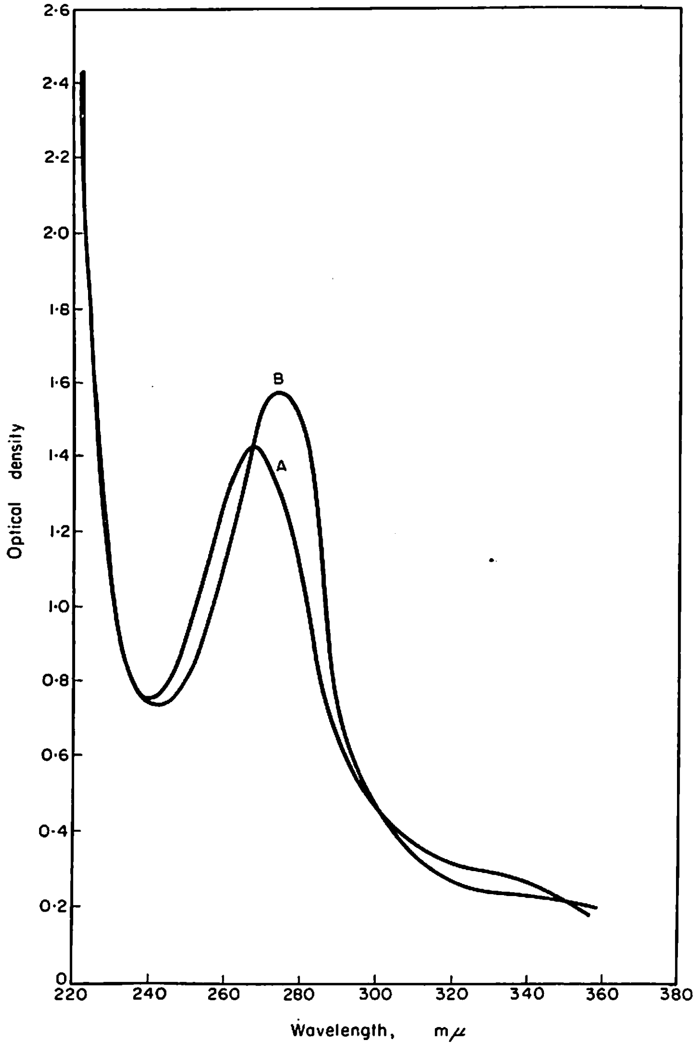

Fig. 1.—Absorption curves for cerium based reagent.
A—5×10^{-6} Mole of cerium chelate in 100 ml of solution, pH 5·2.
B—5×10^{-6} Mole of ternary fluoride complex in 100 ml of solution, pH 5·2.
10-mm light path, measured against water.

optimum conditions the lanthanum reagent was *ca.* 3% more sensitive than the cerium reagent and 20% more sensitive than the lanthanum reaction in aqueous solution at the same pH. The "apparent" pH of these acetone solutions measured on a pH meter was 4·68.

Finally, in this series of experiments, the optimum concentration of acetone was established for the lanthanum based reagent at pH 4·3. The results of this investigation are summarised in Table III and show clearly that the optimum concentration is 25%.

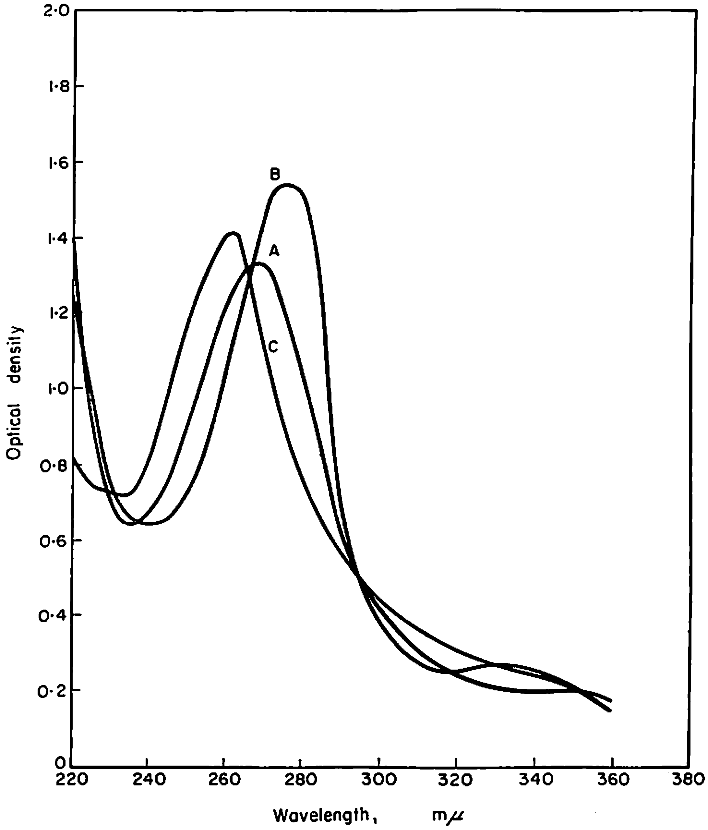

FIG. 2.—Absorption curves for lanthanum based reagent.
A—5 × 10^{-6} Mole of lanthanum chelate in 100 ml of solution, pH 5·2.
B—5 × 10^{-6} Mole of ternary fluoride complex in 100 ml of solution, pH 5·2.
C—5 × 10^{-6} Mole of alizarin complexan in 100 ml of solution, pH 5·2.

Absorption in the ultra-violet region

An examination of the mechanism of the fluoride reaction previously proposed by Leonard and West[1] and observation of absorption spectra of the chelate and ternary complex published in previous papers[1,3] suggests that one would expect to get considerable absorption in the ultraviolet region. Accordingly, the ultraviolet spectra of the exactly formulated 1:1 chelates and 1:1:1 complexes for cerium^{III} (Fig. 1) and lanthanum (Fig. 2) were plotted. These reveal that there is a much stronger absorption in the ultraviolet region and at the wavelength of maximum sensitivity (281 mμ) the lanthanum method is slightly more sensitive (*ca.* 8 %) than the cerium^{III} method. At the optimum pH of 5·0–5·2 the sensitivity of the lanthanum procedure is 200 % greater at 281 mμ than at 620 mμ.

Fig. 3 shows a series of calibration curves drawn up for the lanthanum reagent at pH 5·2 in aqueous solution at 620 and 281 mμ and at 620 mμ and pH 4·3 in a 25 % acetone medium. This last curve flattens out much more markedly than those for the aqueous solutions beyond the upper level of the curve where the Lambert-Beer law is obeyed. It is noticeable also that the projection of these lanthanum curves passes through the origin.

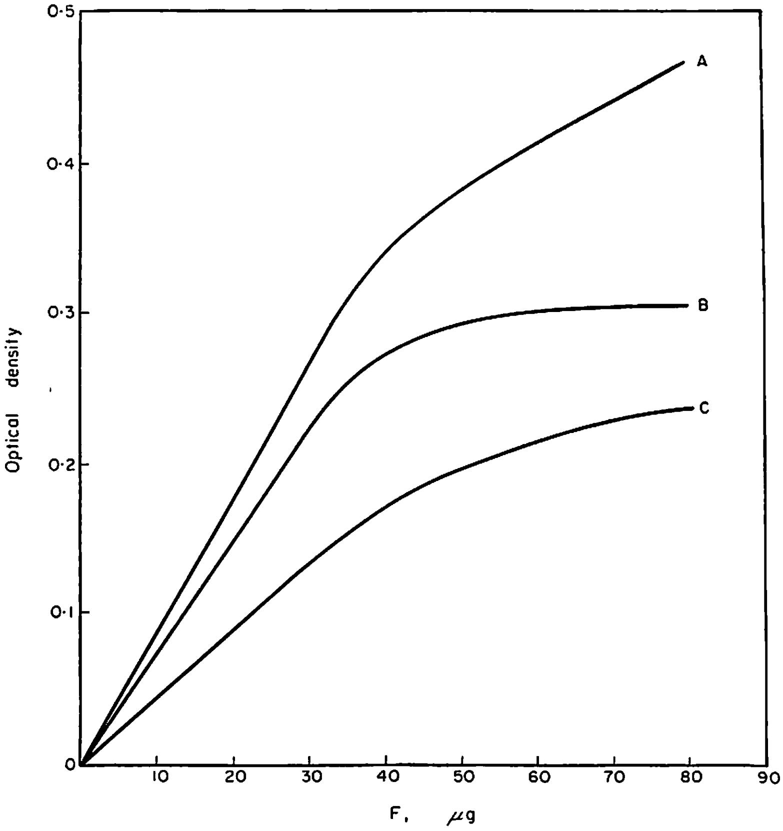

Fig. 3.—Calibration curves for lanthanum reagent.

A—5 × 10^{-6} mole of lanthanum chelate in 100 ml of solution, pH 5·2, 5–100 μg of fluoride, 10-mm silica cell at 281 mμ.

B—5 × 10^{-6} mole lanthanum chelate in 100 ml of 25 % acetone solution, pH 4·3, 5–100 μg of fluoride, 10-mm glass cell at 620 mμ.

C—As A, but using 10-mm glass cell at 620 mμ.

CONCLUSION

The optimum sensitivity of the alizarin complexan method for fluoride is obtained with a lanthanum based reagent operated in aqueous solution at pH 5·0–5·2 with measurements of optical density at 281 mμ. Under these conditions the reaction is 200% more sensitive than that previously reported.[3] Below pH 4·5 the cerium^{III} reagent is slightly more sensitive than the lanthanum reagent. Both are superior to a reagent based on the praseodymium chelate.

EXPERIMENTAL

Reagents

$5 \times 10^{-4}M$ *Solutions of cerium^{III}, lanthanum and praseodymium nitrates*: Prepared by dilution from accurately standardised (EDTA, pH 5·2, Xylenol Orange) 0·02*M* solutions made from "Specpure" materials (Johnson and Matthey).

$5 \times 10^{-4}M$ *Alizarin complexan solution*: *cf.* Reference 3.

Buffer solution (pH 5·0–5·2): 100 g of AnalaR sodium acetate trihydrate + 11 ml of glacial acetic acid dissolved in distilled water and diluted to 1 litre.

Standard fluoride solution: 5 μg of F^-/ml, *cf.* Reference 3.

Apparatus

Hilger "Uvispek" Spectrophotometer, 1-cm silica and glass cells.

Preparation of calibration curves

(A) *Aqueous solution* (620 mμ) *and* (281 mμ): Pipette 10 ml of $5 \times 10^{-4}M$ alizarin complexan solution into a 100-ml graduated flask, then add 2 ml of buffer solution (pH 5·0–5·2) and 1–10 ml of standard fluoride solution. Finally, add, with constant swirling of the contents of the flask, 10 ml of $5 \times 10^{-4}M$ lanthanum nitrate solution and dilute to the mark. Prepare similarly a control solution containing all of the reagents but no fluoride. Set the solutions aside for at least 1·5 hr and measure the optical density of the fluoride solutions in 10-mm cells [silica for 281 mμ, 1 mm slit; glass for 620 mμ, 0·05 mm slit] against the control solution.

(B) 25% *Acetone solution*: As above, but use 2 ml of buffer solution (pH 4·3) and add 25 ml of acetone after the addition of the lanthanum solution.

Analyses of unknowns

Take an aliquot of solution containing from 5–35 μg (5–30 μg for 25% acetone experiments) of fluoride in not more than 78 ml of solution and carry through the above procedure (A).

Note: For routine analytical work it is not necessary to use "Specpure" salts. Normal lanthanum nitrate hexahydrate may be used, but it must be standardised against EDTA, since the composition of the salt may be variable.

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Zusammenfassung—Die Eignung der Alizarinkomplexanchelate von Cer(III), Lanthan und Praseodym zur photometrischen Bestimmung von Mikrogrammengen Fluors wird verglichen. Das Cer(III) reagens zeigt höchste Empfindlichkeit bei pH-Werten unterhalb von 4·5 während das Lanthanreagens pH 5·0 oder höher verlangt. Ein Anstieg der Empfindlichkeit für beide Reagenzien wird beobachtet wenn bei pH 4·3 in 25 volumperzentiger Acetonlösung gearbeitet wird. Die höchste Empfindlichkeit wird mit dem Lanthanreagens erzielt bei pH 5·2 in wässriger Lödung unter Messen bei 28i mμ. Diese Variante ist 200 mal empfindlicher als die Standardmethode bei 620 mμ.

Résume—Les auteurs ont étudié la valeur comparative des chelates du cérium(III), du lanthane et du praséodyme avec l'alizarine comme réactifs pour le dosage spectrophotométrique de quantités de fluorure de l'ordre du microgramme. Le réactif avec le cérium(III) est sensible à pH <4,5 et celui avec le lanthane à pH ≥5,0. On peut augmenter la sensibilité des deux réactifs à pH 4,3 par addition d'acétone à 25%, mais la méthode de dosage la plus sensible est l'utilisation du réactif contenant le lanthane en solution aqueuse à pH 5,2 avec mesure à 281 mμ. Cette méthode est deux fois plus sensible que la méthode standard à 620 mμ.

REFERENCES

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