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Note

Gas chromatography and high-pressure liquid chromatography of commercial hydroxyoxime copper extractants

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Derivatives of hydroxyoximes have been developed specifically for solvent extraction of copper in hydrometallurgical processes in the past few years and their use is increasing steadily. Recently Ashbrook[1] described the composition of the LIX® reagents produced by General Mills (Tucson, Ariz., U.S.A.). These included LIX 64, LIX 64N, LIX 65N, LIX 70, LIX 71 and LIX 73. Separations were performed by column and thin-layer chromatography (TLC) and the structures of the components were determined. The parent compounds are (a) 5,8-diethyl-7-hydroxy-6-dodecanone oxime[2,3], (b) 5-dodecyl-2-hydroxybenzophenone oxime, (c) 2-hydroxy-5-nonylbenzophenone oxime, and (d) 3-chloro-5-nonyl-2-hydroxybenzophenone oxime. The LIX products are composed of the preceding compounds as follows: LIX 63 is (a). LIX 64 is a mixture of (a) and (b), LIX 65N is (c). LIX 64N is a mixture of (a) and (c), LIX 70 of (a) and (d), LIX 71 of (c) and (d), and LIX 73 of (a), (c) and (d). Ashbrook showed by TLC that the aliphatic hydroxyoxime is a minor component when used in mixtures and that the *anti* and *syn* forms of the aromatic hydroxyoximes can be separated.

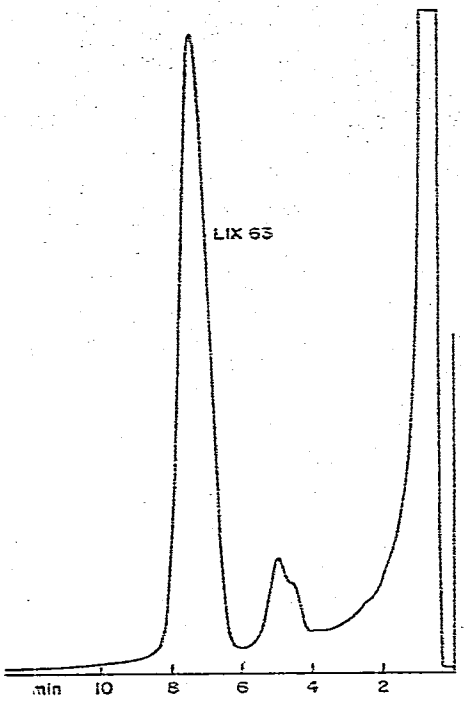
In addition to the LIX reagents there are now available Shell 529® (Shell, Amsterdam, The Netherlands). Acorga P-17® and Acorga P-50® (Acorga, Hamilton, Bermuda). The active ingredient in Shell 529 is 2-hydroxy-5-nonylacetophenone oxime[4] while Acorga P-17 and Acorga P-50 contain 2-hydroxy-5-nonylphenylbenzylketone oxime and 2-hydroxy-5-nonylbenzaldehyde oxime, respectively[5].

This note communicates the applicability of gas chromatography (GC) and high-pressure liquid chromatography (HPLC) to investigations involving commercial hydroxyoxime copper extractants.

EXPERIMENTAL

LIX 63, 64N, 65N, 70, 71, and 73, and Shell 529 and Acorga P-17 were commercial samples.

For GC, *ca.* 25 mg of material was treated with 1 ml of trimethylsilylimidazole reagent Tri-Sil Z (Pierce, Rockford, Ill., U.S.A.) for 10 min and 1-μl samples were injected into a Varian Aerograph Model 1200 gas chromatograph equipped with a flame ionization detector. The column was 5 ft. × 1/8 in. O.D. stainless steel packed with 5% SE-30 on Chromosorb W AW DMCS, 60–80 mesh. The carrier gas (nitrogen) flow-rate was 50 ml/min. The aliphatic hydroxyoxime LIX 63 was chromatographed



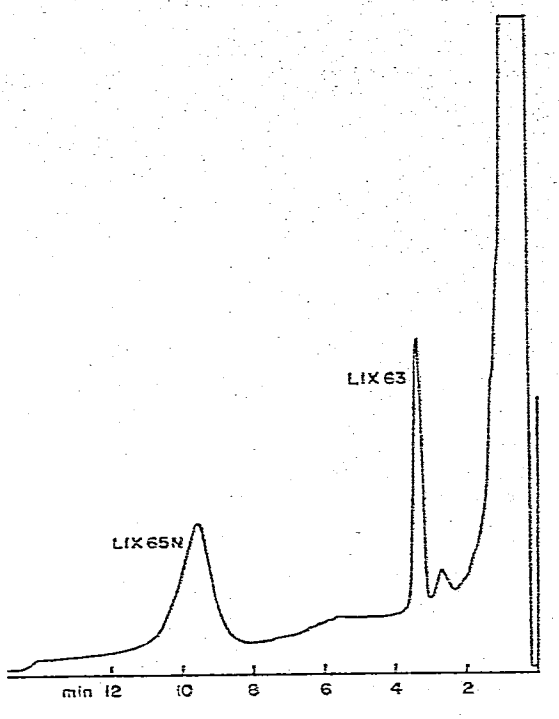
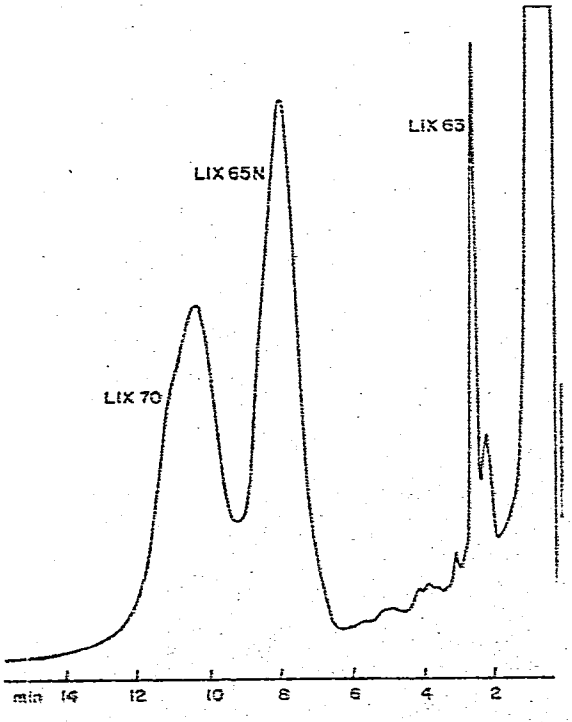


Fig. 1. GC of LIX 63.
Fig. 2. GC of LIX 64N.



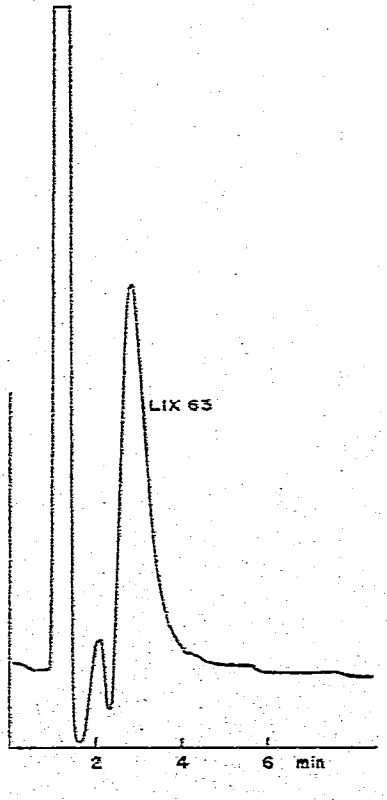


Fig. 3. GC of LIX 73.
Fig. 4. HPLC of LIX 63 with refractive index detector.

at 170° while mixtures of aliphatic and aromatic LIX reagents were separated by linear temperature programming at 4°/min from 170° to 225°. Temperatures for Shell 529 and Acorga P-17 were 200° and 225°, respectively.

For HPLC a Waters Assoc. Model ALC 202 instrument with ultraviolet (254 nm) and refractive index detectors was used. The packing was Durapak Carbowax 400 on Porasil C in a 2 ft. × 1/8 in. O.D. column. For LIX 63 the solvent was 2,2,4-trimethylpentane–chloroform (11:3) at a flow-rate of 2.0 ml/min while for the other extractants the solvent was pentane–chloroform (10:3) at 2.0 ml/min. Generally 5-μl samples were injected using 10% solutions of LIX 63 and 1% solutions of the other extractants.

RESULTS AND DISCUSSION

Some typical GC separations are shown in Figs. 1, 2 and 3 for LIX 63, LIX 64N and LIX 73, respectively. The procedure is particularly effective for LIX 63 which is a minor but important component of LIX 64N, LIX 70 and LIX 73, as reported by Ashbrook. The GC procedure readily separates the aliphatic oxime (a) and two aromatic oximes (c) and (d) which are in currently marketed LIX reagents. The hydroxyoxime in Shell 529 had a retention time of 4 min at 200°, while Acorga P-17

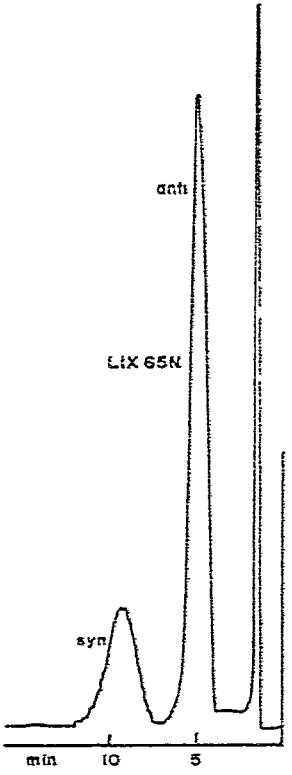


Fig. 5. HPLC of LIX 65N.

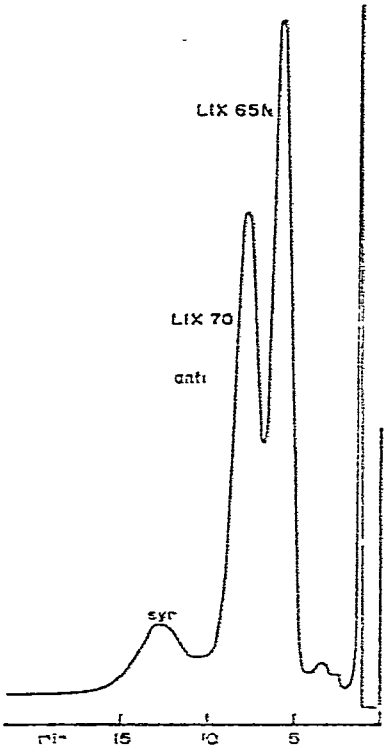


Fig. 6. HPLC of LIX 71.

appeared at 6 min at 225°. The volatility of the Shell 529 extractant is between that of LIX 63 and LIX 65N in accord with its mixed aromatic–aliphatic structure. Under the conditions used, Acorga P-17 is not separated from LIX 65N. The *anti* and *syn* isomers of the hydroxyoximes also are not separated by the GC procedure.

HPLC separations are shown in Fig. 4, 5 and 6 for LIX 63, LIX 65N and LIX 71, respectively. For LIX 63, the refractive index detector was used while the aromatic hydroxyoximes were detected by ultraviolet (UV). The *anti* and *syn* isomers of the aromatic hydroxyoximes are well separated (Fig. 5) and the mixed nature of LIX 71 is clearly indicated (Fig. 6). The major (*anti*) isomers of the hydroxyoximes in Shell 529 and Ocorga P-17 have retention times of 5 min and 10 min, respectively. The ability of HPLC to separate and analyse *anti* and *syn* isomers easily and rapidly is useful in investigations since the isomers differ in their chelating properties. HPLC has the advantage of separating extractants directly without prior conversion to derivatives. The separation of isomeric oximes by HPLC may be added to the previously reported techniques of column adsorption chromatography[6] and TLC[7].

ACKNOWLEDGEMENT

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