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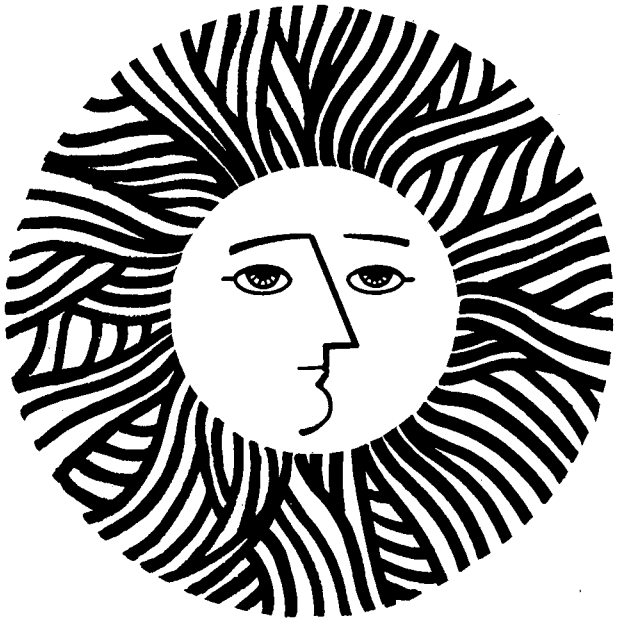

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LBID461

Metal Coordination Chemistry: Removal and Recovery of Metals From Heavy Crude and Shale Oils with Multidentate Ligands

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Introductions

The biogeochemical origin of the inorganic arsenic and organoarsenic compounds we have previously identified[1] has been important to elucidate in order to determine whether these arsenic compounds have been synthesized or released during oil shale retorting.

We recently extracted a Green River Formation Oil Shale Kerogen (NBS standard) with methanol and tentatively determined, using the HPLC-GFAA combination, that phenylarsonic acid and arsenate were present in the kerogen sample. In this quarterly, we present evidence that unequivocally identifies phenylarsonic acid in the extract and strengthens our earlier postulate that multidentate ligands can remove these compounds from shale oil or retort waters.

We have also made substantial progress in defining the use of multidentate ligands for the removal of vanadyl ion (VO^{2+}) from its indigeneous state i.e. complexed to porphyrin and non-porphyrin ligands.

Speciation Studies of Organoarsenic and Inorganic Arsenic Compounds in Oil Shale Kerogen.

In order to determine whether our tentative assignment of phenylarsonic acid in an oil shale kerogen extract was in fact correct, we utilized the facile reaction of this organoarsenic compound with 3-methylcatechol and identified the five coordinate derivative by GC-EIMS.

Thus, the total methanolic extract was distilled and the residue dried under vacuum for several days to remove any traces of water. The residue was completely soluble in benzene and to this solution was added an excess amount of 3-methylcatechol. After refluxing for three hours the reaction mixture was extracted with sodium bicarbonate to remove excess catechol. The benzene layer was dried and distilled to a volume of ~100 μl.

This solution was analyzed by capillary column gas chromatography with the known derivative and ascertained that it was indeed present in the derivatized extract. The phenylarsonic acid•3-methyl catecholate was examined by GC-EIMS and its retention time coincided with the known compound. More importantly, the mass spectrum was also identical to the known sample. Pertinently, the ions at m/e 274 and m/e 197 were evident.

Figure 1 shows the known compound's EIMS while Figure 2 shows the EIMS of the organoarsenic compound we identify in the methanolic extract as the phenylarsonic acid•3-methylcatecholate. Figures 3-5 provide the reconstructed ion chromatographs (RIC) and shows that single ion monitoring clearly defines the peak at scan 805 (cis) and its isomer at scan 825 (trans) as identical to the known compound (m/e 274).

We believe this important discovery to be the first identification of any organoarsenic compound in a fossil source and demonstrates the potential of multidentate ligands as viable candidates in the removal of inorganic arsenic and organarsenic compounds from fossil fuel products such as shale oil or retort waters.

Competition Experiments Between Vanadyl Etioporphyrin and Multidentate Ligands

We have continued our competition experiments, designed to remove vanadyl ion from porphyrins, using vanadyl etioporphyrin as an example of a vanadyl porphyrin present in heavy crude oils with various multidentate ligands. The two methods used to follow these equilibria were UV-VIS spectroscopy and HPLC-GFAA analysis. Figure 6 shows the UV-VIS spectrum for salen, a representative multidentate ligand, in its competitive equilibrium with vanadyl etioporphyrin in p-xylene (1,4-dimethylbenzene) at 140°C for 48 hr.

These competitive equilibria occur only in the presence of air and are not evident when conducted under a nitrogen atmosphere. Additionally, $EtioH_2$ decomposes in air and not under nitrogen. These factors are important in future removal studies and again seem to indicate the potential of multidentate ligands in removing vanadyl ion from its indigeneous state.

Future Work

Studies on the speciation of arsenic compounds in shale oil continues with the National Bureau of Standards group, while similar studies on heavy crude oils for both vanadyl porphyrin and non-porphyrins continues at LBL. Studies involved in the removal of arsenic compounds from shale oils will be initiated and the competitive removal of vanadyl ion will also be pursued.

Acknowledgement

We wish to thank the continuous efforts of the NBS group (Drs. Brinckman and Weiss), under our colaborative speciation program, for the oil shale extractions. We also acknowledge John Komlenic and Raja Tannous for experimental results.

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1. R. H. Fish, F. E. Brinckman and K. L. Jewett, Environ. Sci. Tech. 1982, in press.
2. C. S. Weiss, K. L. Jewett, F. E. Brinckman and R. H. Fish, National Bureau of Standards Special Publication 618 197 (1981).

Presentation and Publication

J. Komlenic and R. H. Fish. Petroleum Geochemistry Symposium at the National ACS meeting to be held in Las Vegas, NV, March 29-April 2, 1982. Presentation on the speciation of vanadyl porphyrin and non prophyrin compounds in heavy crude oils and the competitive removal of vanadyl ion (VO^{2+}) with multidentate ligands.

C. S. Weiss, K. L. Jewett, F. E. Brinckamn and R. H. Fish. "Application of Molecular Substituent Parameters for the Speciation of Trace Organometals in Energy-Related Process Fluids by Element-Selective HPLC, National Bureau of Standards Special Publication 618, p. 197 (1981).

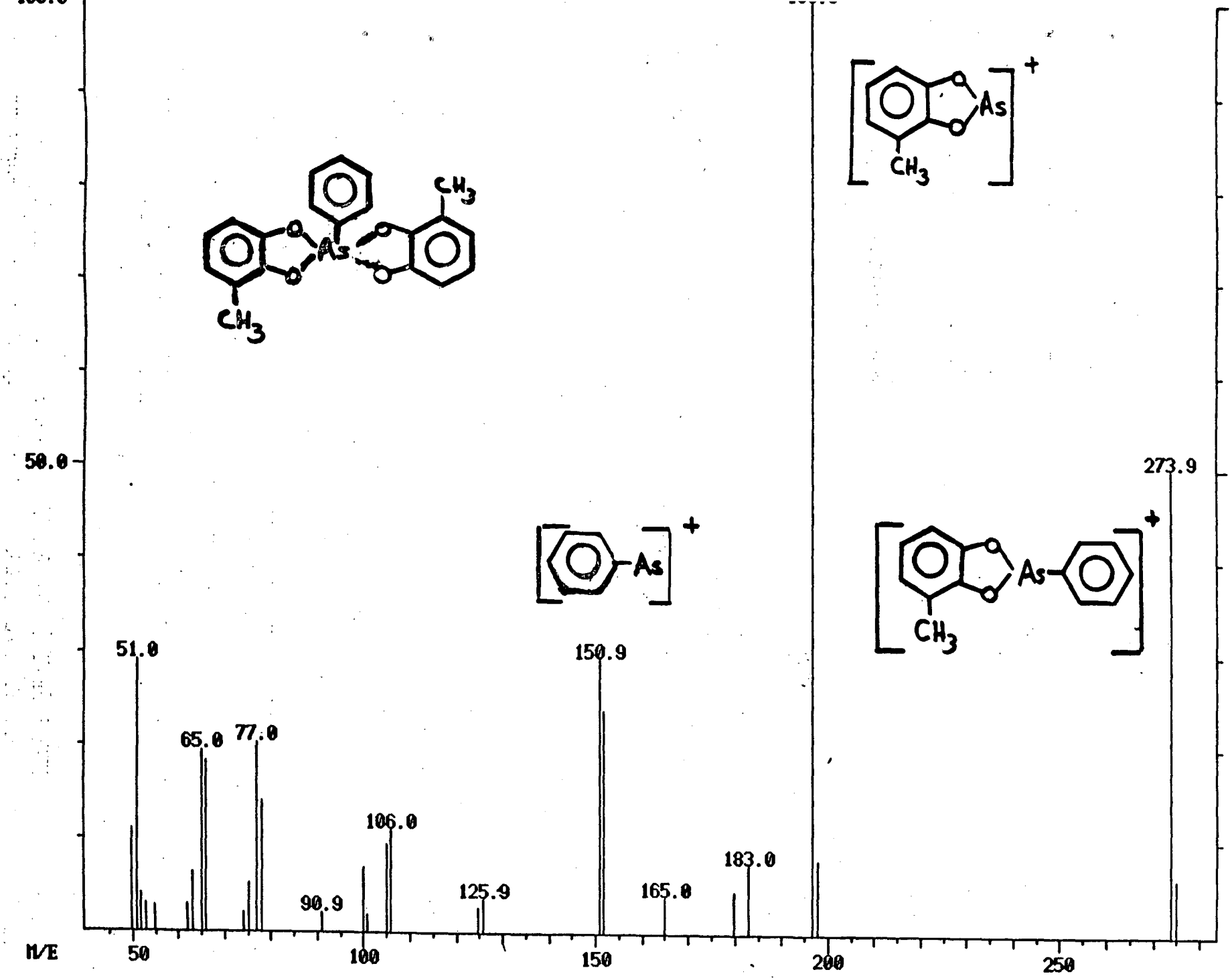


Figure 1. GC-EIMS of the phenylarsonic acid·3-methylcatecholate.

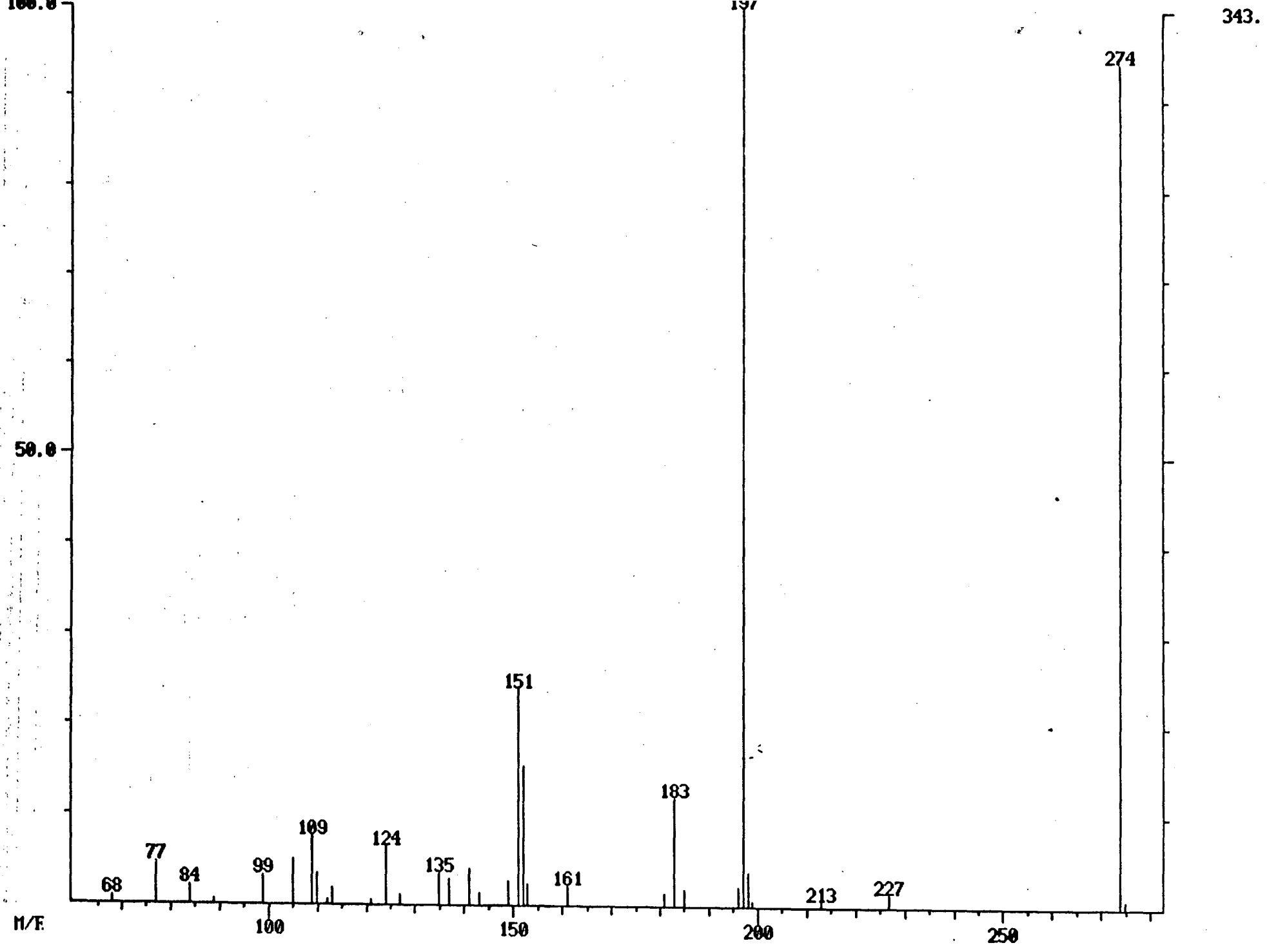


Figure 2. GC-EIMS of unknown arsenic derivative extracted from oil shale kerogen.

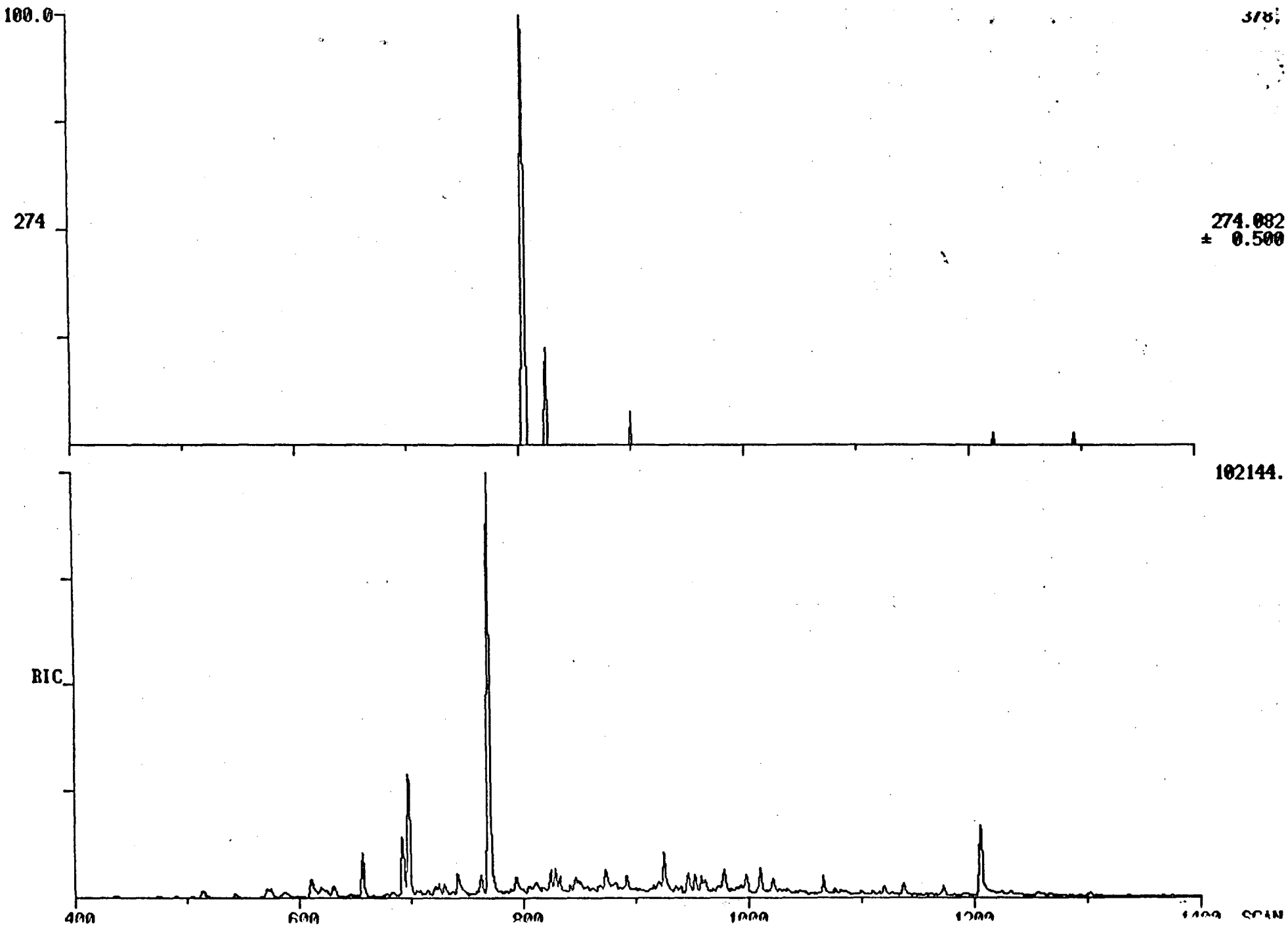
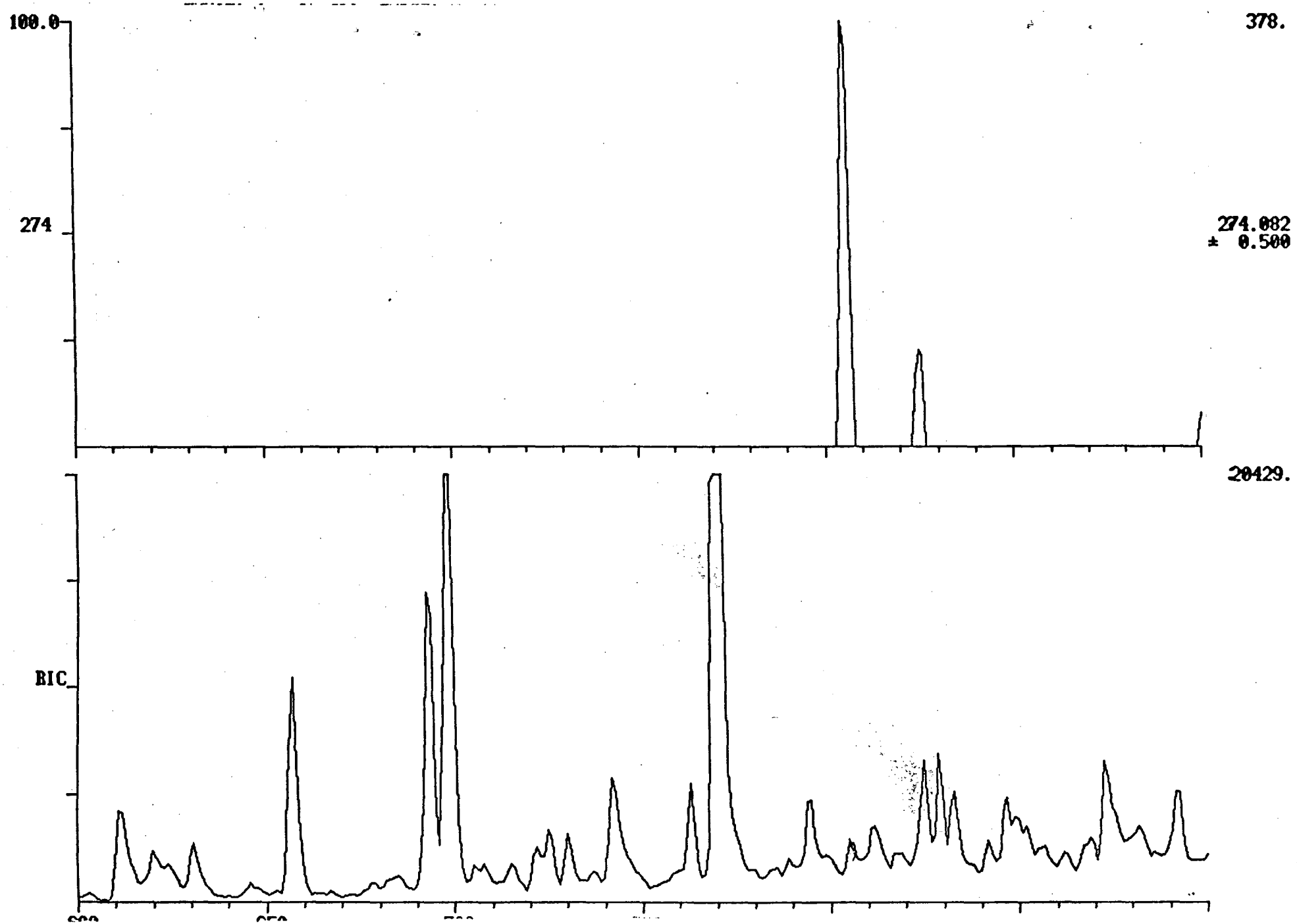


Figure 3. Reconstructed ion chromatogram of the extract and the selective ion (m/e 274) monitoring of those compounds with characteristic EIMS of known catecholate.



Fiugure 4. Similar to Figure 3 expanded.

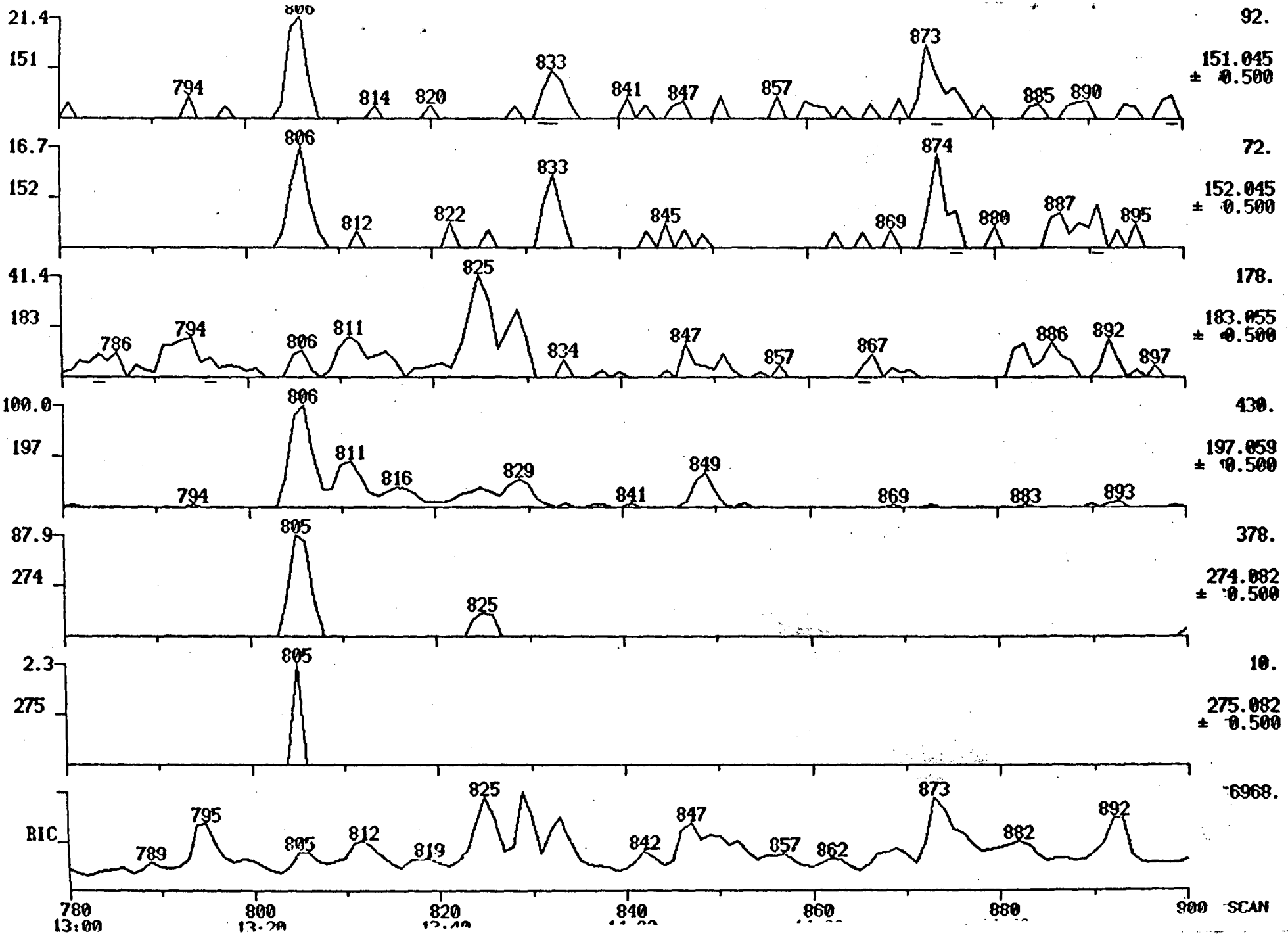


Figure 5. Selective ion monitoring, m/e 274 and m/e 197, of compounds in the extract.

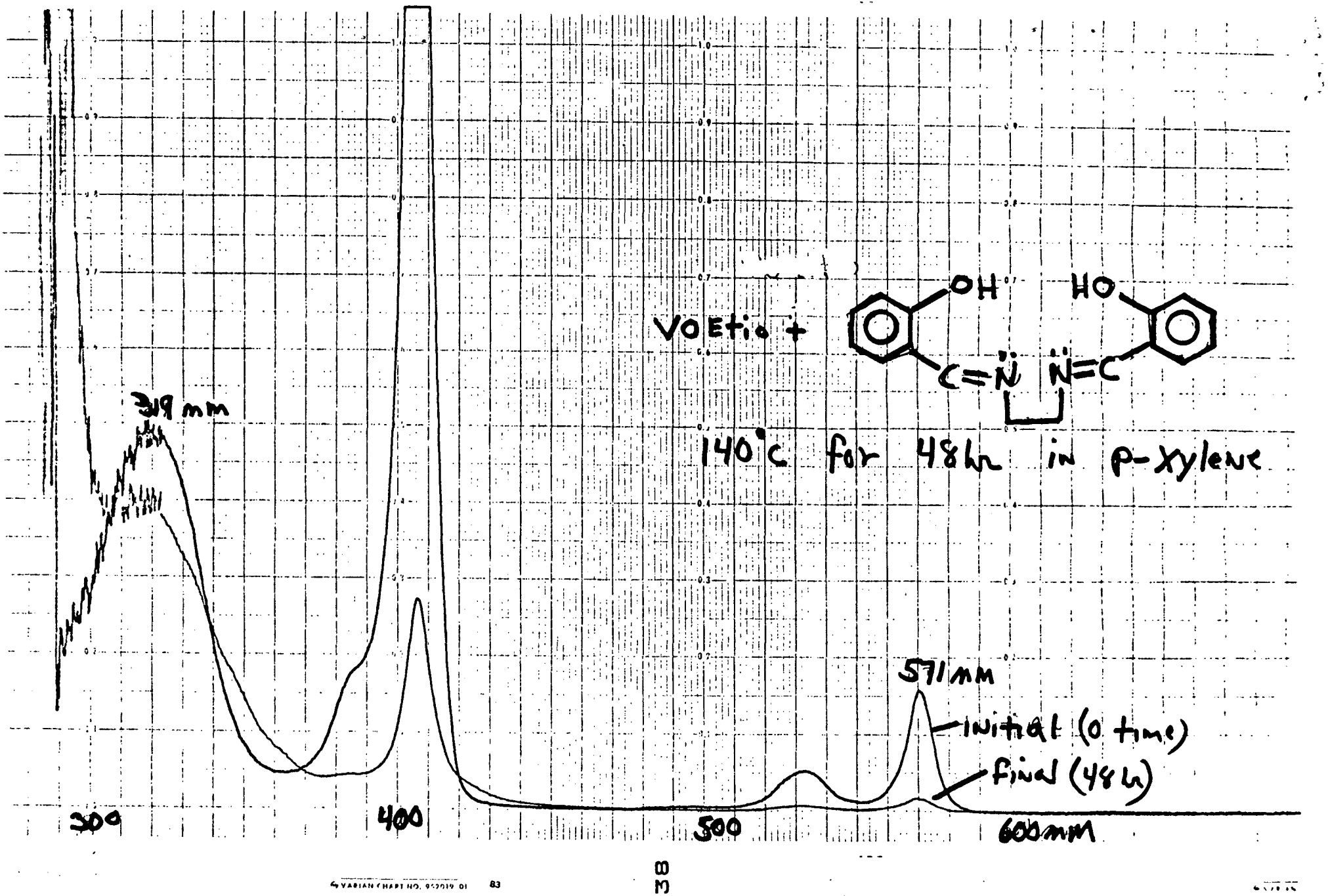


Figure 6, UV-VIS spectrum of EtioVo and salen competition.

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