

# DIFFERENTIATION OF MONOLAYER AND MULTILAYER COVERAGE OF THIOL COLLECTORS ON METAL SULFIDES BY MEANS OF ToF-SIMS

Siew Wei Goh<sup>a</sup>, Alan N Buckley<sup>a</sup>, Robert N Lamb<sup>a</sup>,  
Ronald Woods<sup>b</sup>

<sup>a</sup> School of Chemical Sciences, The University of New  
South Wales, Sydney, NSW 2052, Australia

<sup>b</sup> School of Science, Griffith University, Nathan,  
Qld 4111, Australia

In research on the interaction of mineral surfaces with flotation collectors, there is often the need to establish whether adsorption has been limited to a monolayer, or whether a multilayer species has also been formed. In the particular case of metal sulfide surfaces modified by the adsorption of thiols such as alkyl dithiophosphates or xanthates, it is necessary to determine whether only the chemisorbed monolayer has been formed, or whether the corresponding dithiolate or metal thiolate is present on top of the chemisorbed layer.

For some metal sulfides, and thiols containing no other heteroatoms such as phosphorus, sulfur core electron binding energy differences allow X-ray photoelectron spectroscopy (XPS) to be used to confirm the presence of adsorbed collector. Metal core level XPS and X-ray excited Auger electron spectroscopy can then be used to differentiate monolayer from multilayer coverage [1,2]. In some cases, however, this is not possible because thiol and metal sulfide sulfur core electron binding energies are similar, and a more generally applicable surface characterisation technique is required. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), which has a surface sensitivity superior to that of XPS, has been used to a limited extent over the past decade to detect the presence of adsorbed collectors on mineral surfaces [e.g. 3-6]. In principle, ToF-SIMS should be able to effect the differentiation between monolayer and multilayer coverage, but for some of the sulfide mineral/thiol collector systems investigated, intact metal-thiol secondary ions have been observed, whereas for others, the thiol parent ion has been the heaviest collector-related ion detected [5]. Thus it cannot be assumed *a priori* that static SIMS can be used to effect the differentiation sought.

In this work, experiments were carried out to establish whether ToF-SIMS is able to differentiate monolayer and multilayer coverage of thiol collectors on metal sulfides. The systems investigated were those for which XPS is able to provide an independent determination of the extent of coverage, and included diethyldithiophosphate (DTP) on chalcocite, DTP on Ag<sub>2</sub>S prepared by sulfidising metallic silver, and *iso*-butyl xanthate (BX) on galena. Collector coverage on the surface of each single-piece mineral specimen was controlled by adjusting the thiol solution concentration and interaction time. Both positive and negative secondary ion mass spectra were obtained. The spectra could be determined only at ambient temperature, consequently the presence of any volatile dithiolates such as dioxanthogen might not have been detected.

For the chalcocite/DTP system, a strong DTP<sup>-</sup> peak was observed for both monolayer and multilayer coverage, and relative to the intensity of that peak, the intensity of the doublet corresponding to <sup>63</sup>CuDTP<sup>-</sup> and <sup>65</sup>CuDTP<sup>-</sup> ions for the multilayer was a factor of 2 greater than that for the monolayer. The intensity of the CuDTP<sup>+</sup>

doublet was low but comparable for both monolayer and multilayer coverage. These observations were only partly in accord with expectation, as it is generally agreed that the monolayer species is DTP chemisorbed to Cu in the surface of the chalcocite lattice, and previous XPS studies have suggested that under similar E<sub>h</sub> conditions, the multilayer species is adsorbed CuDTP. Thus, CuDTP ions were expected to be significantly more numerous for multilayer rather than monolayer coverage. The most surprising observation, however, was the Cu(DTP)<sub>2</sub><sup>-</sup> doublet evident for multilayer (but not monolayer) coverage, as the presence of Cu(DTP)<sub>2</sub><sup>-</sup> ions indicated the multilayer species was predominantly Cu(DTP)<sub>2</sub> rather than CuDTP. Although there has been previous electrochemical evidence for the formation of Cu(DTP)<sub>2</sub> on copper sulfide [7], Cu 2p photoelectron spectra and S 2p:Cu 3s intensity ratios have revealed neither the presence of Cu(II) nor the Cu(DTP)<sub>2</sub> stoichiometry in the multilayer species [e.g. 2].

Analogous observations were made for the Ag<sub>2</sub>S/DTP system. In particular, positive and negative ions corresponding to AgDTP were observed for monolayer coverage. A relatively intense doublet from the Ag(II) species <sup>107</sup>Ag(DTP)<sub>2</sub><sup>-</sup> and <sup>109</sup>Ag(DTP)<sub>2</sub><sup>-</sup> was observed from the multilayer but not the monolayer. These observations provide strong evidence in support of Ag(DTP)<sub>2</sub> being one, if not the only, multilayer species at high E<sub>h</sub> for the Ag<sub>2</sub>S/DTP system.

For the PbS/BX system, intact PbBX<sup>+</sup> (but not PbBX<sup>-</sup>) ions were observed for monolayer coverage. For multilayer coverage, intact Pb(BX)<sub>2</sub><sup>-</sup> or Pb(OH)BX<sup>-</sup> ions were not detected, and positive ion peaks corresponding to Pb(BX)<sub>2</sub> were small. Some Pb-containing negative ions of m/z > 357 (heavier than PbBX) were observed even for monolayer coverage, indicating that ions such as those at m/z 393 from S<sub>2</sub><sup>208</sup>PbS<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub><sup>-</sup>, originated from chemisorbed BX and S<sub>2</sub>Pb from the lattice rather than from multilayer Pb(BX)<sub>2</sub>. However, ions at m/z 451 and 427 could be assigned only to fragments of Pb(BX)<sub>2</sub>.

It can be concluded from the findings reported here that ToF-SIMS provides information complementary to that obtained by XPS, and in some cases can differentiate monolayer from multilayer coverage. However, it is not yet possible to assert that ToF-SIMS alone can always allow this differentiation. In the case of DTP adsorption, if the multilayer species had been the metal monothiolate only (*i.e.*, if the metal dithiolate had not been involved), then it is unlikely that ToF-SIMS would have been able to provide an unequivocal differentiation of the two coverage conditions.

- [1] A.N. Buckley, R. Woods, *Int. J. Miner. Process.*, **28**, 301 (1990).
- [2] A.N. Buckley, R. Woods, *Electroanal. Chem.*, **357**, 387 (1993).
- [3] J.S. Brinen, F. Reich, *Surf. Interface Anal.*, **18**, 448 (1992).
- [4] J.S. Brinen, S. Greenhouse, D.R. Nagaraj, J. Lee, *Int. J. Miner. Process.*, **38**, 93 (1993).
- [5] D.R. Nagaraj, J.S. Brinen, *Trans. Indian Inst. Met.*, **50**, 365 (1997).
- [6] A.N. Buckley, B. Gong, R.N. Lamb, R. Woods, in *Proc. Int. Symp. Electrochemistry in Mineral and Metal Processing V*, R. Woods and F.M. Doyle Editors, PV 2000-14, p.72, Electrochem. Soc., Pennington, NJ (2000).
- [7] S. Chander, D.W. Fuerstenau, *J. Electroanal. Chem.*, **56**, 217 (1974).