

## MASS SPECTROMETRY OF METAL-CARBONYL CLUSTERS ON A BRUKER MICROTOF

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Mass spectrometric analysis of metal-carbonyls is a valuable aid to synthesis and characterisation. The smaller neutral examples are volatile and have been examined using conventional Electron Impact ionisation for many years [1]. However for larger clusters and derivatives thermal instability and lower volatility becomes a problem. Some limited success was achieved with FAB ionisation, but the low basicity of carbonyl groups hindered chemical ionisation processes [2] and the harshness of the method led to extensive fragmentation.

The introduction of ElectroSpray Ionisation (ESI) suggested a potentially valuable technique, since natural volatility is not a limiting factor. However chemical ionisation was still difficult until the introduction of NaOMe as an ionisation aid was introduced [3]. This converted the neutral metal-carbonyl compounds to  $[M+OMe]^-$  and/or  $[M+Na]^+$  ions which could be readily detected.

This new technique was found to be very machine dependent. Whereas excellent spectra were generally available on a Fisons Platform II electrospray spectrometer, signals were very difficult to obtain from a Finnegan LCQ, presumably because the heated-capillary desolvation process used therein decomposed the thermally-labile ions.

We have recently acquired a Bruker MicrOTOF machine, and have found that this is suitable for analysis of metal-carbonyl compounds using the NaOMe derivatisation, providing gentle conditions were employed. Unfortunately, under these same conditions the signals from the sodium formate calibration mixture (necessary for high precision mass measurement) became indistinct.

We have now identified a series of metal carbonyl compounds that can be used as a mixture to provide accurate calibration [see Table]. These compounds fulfil the criteria that they: (i) span a useful mass range; (ii) are reasonably air-stable; (iii) derivatise readily with NaOMe; (iv) do not undergo significant fragmentation.

| Compound                           | Mass of $[M+OMe]^-$ ion | Compound                           | Mass of $[M+OMe]^-$ ion |
|------------------------------------|-------------------------|------------------------------------|-------------------------|
| Mo(CO) <sub>6</sub>                | 296.8933                | W(CO) <sub>6</sub>                 | 382.9388                |
| Mn <sub>2</sub> (CO) <sub>10</sub> | 420.8436                | Re <sub>2</sub> (CO) <sub>10</sub> | 682.8768                |
| Os <sub>3</sub> (CO) <sub>12</sub> | 938.8368                | Ir <sub>4</sub> (CO) <sub>12</sub> | 1136.8074               |

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