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X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS OF CLEANING PROCEDURES FOR SYNCHROTRON RADIATION BEAMLINE MATERIALS AT THE ADVANCED PHOTON SOURCE

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ABSTRACT

TZM (a high temperature molybdenum alloy), machinable tungsten, and 304 stainless steel were cleaned using environmentally safe, commercially available cleaning detergents. The surface cleanliness was evaluated by x-ray photoelectron spectroscopy (XPS). It was found that a simple alkaline detergent is very effective at removal of organic and inorganic surface contaminants or foreign particle residue from machining processes. The detergent can be used with ultrasonic agitation at 140 °F to clean the TZM molybdenum, machinable tungsten, and 304 stainless steel. A citric-acid-based detergent was also found to be effective at cleaning metal oxides, such as iron oxide, molybdenum oxide, as well as tungsten oxides at mild temperatures with ultrasonic agitation, and it can be used to replace strong inorganic acids to improve cleaning safety and minimize waste disposal and other environmental problems. The efficiency of removing the metal oxides depends on both cleaning temperature and time.

INTRODUCTION

The Advanced Photon Source (APS), currently under construction at Argonne National Laborotary (ANL), will be one of the most powerful synchrotron x-ray photon sources in the world. The beamline sections where the x-rays will be transported will contain high-thermal-load ultrahigh-vacuum (UHV) compatible components. These components are made of 304 or 316 stainless steels (for UHV component joints, vacuum chambers, and bellows), TZM high-temperature molybdenum alloy (for slits and beam position monitor blades), and tungsten (for safety photon shutters). Before any of these components can be assembled, they must be cleaned to remove surface contaminants so that the ultrahigh vacuum necessary for successful operation can be achieved. Fabrication of the components will also involve joining processes, such as explosion and diffusion bonding, brazing, and soldering, etc. Removal or minimizing of surface

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DISCLAIMER

oxides of the joining materials is crucial to obtain secure bonding. Although many cleaning procedures have been developed for stainless steels [1-3], most of them involve the use of chemicals that present environmental, safety, and waste disposal concerns. Recommended cleaning procedures of refractory metals, such as machinable tungsten and molybdenum, use strong acids or molten salt baths, such as molten (750-850 °F) soda containing some sodium nitrite ($NaNO_2$), boiling 20% KOH solution, or a mixture of nitric and sulfuric acids for cleaning or pickling TZM molybdenum and molten $NaNO_2$ or NaOH for cleaning tungsten [3-4].

A growing concern for present-day vacuum scientists and engineers is finding alternative, environmentally safe, and healthy ways of cleaning components for UHV systems. For large vacuum systems, such as accelerator storage rings and beamlines, the problems caused by using conventional cleaning approaches, such as solvents, strong acids, and strong bases, are magnified. At the APS, studies directed at finding alternative environmentally safe cleaners for UHV storage rings and beamlines were undertaken, and several important results were achieved. For example, extruded 6063 aluminum tubing and 2219 aluminum flanges were used to make the 1100-meter-circumference main storage ring for the APS. Traditional techniques for cleaning aluminum usually involve degreasing in solvents, followed by a strong alkaline etching [5]. Auger electron spectroscopy (AES) and XPS studies have suggested that 6063 and 2219 aluminum could be cleaned by a mild alkaline detergent rather than the strong alkaline detergents [6-7]. The cleaning procedures were employed to clean all APS storage-ring aluminum components and a base pressure of $<1\times10^{-10}$ Torr has been achieved [8]. Studies on liquid/supercritical fluid carbon dioxide cleaning of stainless steels, OFHC copper, and Al_2O_3-copper were also investigated [9].

In this paper, we present results of surface analysis, using XPS, of TZM molybdenum, machinable tungsten, and 304 stainless steel following treatment with commercially available chemical cleaners that pose very little risk to either the environment or safety.

EXPERIMENTAL

The XPS measurements were performed in an ultrahigh vacuum chamber at an operating pressure of $\sim5\times10^{-9}$ torr using a Perkin Elmer model 04-548 Mg Kα x-ray source and a model 10-360 spherical capacitor electron energy analyzer. The bonding energy scale was not calibrated for each spectrum so the absolute energies of the peaks are estimated to be accurate to ±0.5 eV.

Table 1 shows the materials used for the cleaning tests. TZM molybdenum and machinable tungsten were cut to 12×12×2 mm coupons using electrical discharge machining (EDM), and 304 stainless steel was machined to the same size. Before cleaning, all coupons were polished by hand using 400-grit SiC paper that simulates a grinding process.

The cleaners that were evaluated are listed in Table 2. Solvents (acetone and methanol) were used at room temperature with ultrasonic agitation for 10 minutes for each step. All other cleaners were used at 140 °F with ultrasonic agitation for 10 to 15 min. To evaluate the effect of temperature on surface cleanliness of 304 stainless steel, 3% Citranox was also tested at room temperature and 110 °F. Following the cleaning procedures, all samples were rinsed with deionized water and blown dry with nitrogen. At least three samples were measured for each cleaning procedure. All samples were kept in a clean-room environment overnight prior to XPS measurements.

Table 1. Cleaning Test Materials

Materials	Manufacturer	Main Chemical Composition (wt%)
TZM molybdenum	The Rembar Company, Inc	99% Mo, 0.5Ti-0.1Zr-0.02W
machinable tungsten	Mi-Tech Metals, Inc	95% W balance Ni, Cu, and Fe
304 stainless steel		18-20% Cr, 8-10% Ni, 2% Mn, balance Fe

Table 2. Commercial Cleaners

Cleaner Name	Almeco 18	Detergent-8	Citranox	Solvents
Manufacturer	HENKEL Corp.	Alconox, Inc.	Alconox, Inc.	Fisher, Inc.
Chemical Family	Powder Alkaline Detergent	Liquid Alkaline Detergent	Liquid Acid Detergent	Solvent
Known Ingredients	Tetrasodium, Pyrophosphate, Sodium, Tetraborate	Alkanol Amine, Dipropylene Glycol Methyl Ether	Citric Acid, Hydroxyacetic Acid	Acetone and Methanol
Application (by Manufacturer)	Removal of oils and light oxide of aluminum	Removal of oil, resin, and rosins; Ideal for cleaning circuit board and electronic parts	Removal of scale, milkstone, metal oxides, fats, oils, greases	Removal of greases and fats
Operation (by Manufacturer)	Automatic	Manual or Ultrasonic;	Manual or Ultrasonic;	
Waste Disposal (by Manufacturer)	Readily Disposable	Readily Disposable	Readily Disposable	Waste Treatment
Concentration (%)	2-4 % (wt%)	2-4 % (vol%)	2-4 % (vol%)	100 %
PH Value	9.0-9.4	10.8-11.1	2.7-3.1	

RESULTS AND DISCUSSION

1. 304 Stainless Steel

Survey XPS spectra (0-1100 eV binding energy) were taken for each sample. In order to measure the effectiveness of the cleaners for removing organic-based residues, the spectra were analyzed for iron, chromium, nickel, carbon, and oxygen by measuring the areas of the corresponding peaks. Using published sensitivity factors [10], these peak areas were converted into percentage concentration on the sample surfaces, and the results are shown in Figure 1. It can been seen from this figure that cleaning by solvents left over 50% carbon concentration on the surface, while only a small trace of chromium and no nickel were found. Of the cleaners tested, Almeco 18 is very effective at removing carbon, while Citranox left more metals, such as Cr and Ni, on the surface except for Fe (this will be discussed later). Cleaning of stainless steel, first with Citranox at 140 °F for 10 min then by Almeco 18 at 140 °F for 10 min, was also studied, and it was shown that this combination is the most effective at removing carbon as well as maximizing the metal concentrations on the surface.

In addition to carbon removal, an effective cleaner should remove other surface contaminants and inorganic particulates. Evaluation of the cleaners for these attributes was done by analyzing the XPS spectra in the lower energy region (binding energy from 0-180 eV). Spectra in this energy range are shown in Figure 2. From this figure, it is seen that solvent cleaning did little to remove inorganic particulates, such as Si, S, and Ca (at ~439 eV). A small trace of Si and no S, P, and Ca were found on the sample cleaned by Citranox. No trace of Si, S, P, and Ca were found on the samples cleaned by Almeco 18 and a combination of Citranox and Almeco 18. A clear Ni spectrum was observed on the samples cleaned by Almeco 18, Citranox, and their combination, and it was not found on the samples cleaned by Detergent-8 and solvents.

The effectiveness of the cleaners for thinning the oxide layers is evaluated by analysis of the Fe $2p_{3/2}$ spectrum at ~715 eV (shown in Figure 3). A definitive Fe 2p spectrum was not observed on the samples cleaned by solvents. For the samples cleaned by Detergent-8 and Almeco 18, a strong iron oxide (Fe_2O_3) peak at ~710.7 eV [12] was seen. The iron oxide peak shifted to ~706 eV (metal) for the sample cleaned by Citranox. A thin iron oxide layer was also observed in the sample cleaned by the sequence of Citranox and Almeco 18 (for 10 min at 140 °F). It may be necessary to clean for longer period (15-20 min) for Citranox to effectively remove a heavy iron oxide layer.

In order to evaluate the effect of cleaning temperature on surface cleanliness, 304 stainless steel samples were also cleaned by Citranox at room temperature and 110 °F for 15 min. Figure 4 shows the Fe $2p_{3/2}$ spectrum at ~715 eV cleaning at three different temperatures. These results indicate that the iron oxide (Fe_2O_3) layer was still as thick then cleaning at room temperature. The iron oxide layer became thinner as the cleaning temperature increased from room temperature to 110 °F. As temperature increased to 140 °F, a clear metal Fe $2p_{3/2}$ appeared at ~706 eV.

2. Machinable Tungsten

The spectra were analyzed for carbon, oxygen, tungsten, copper, and nickel by measuring the areas of the corresponding peaks from survey XPS spectra, and the results are shown in Figure 5. It can be seen that the combination of Citranox and Almeco 18 is the most effective at carbon removal, and the highest surface concentration of tungsten was seen on the sample cleaned by Citranox. Figure 6 shows XPS spectra in the low energy region, and it can be seen that the cleaner Almeco 18 was very effective at removing inorganic materials such as Si (most likely SiC particle residue from abrasive grinding). Solvents did a relatively poor job, and a trace of Si was found on surfaces cleaned by Detergent-8 and Citranox.

Figure 7 shows W 4f spectra at ~32 eV. Of the cleaners tested, Almeco 18 and especially Citranox are the most effective at removing tungsten oxide and maximizing metallic tungsten. The samples cleaned by solvents and Detergent-8 showed two additional peaks between 35 eV to 39 eV due to tungsten oxides (most likely WO_3 or $NiWO_4$) on the surfaces. The sample cleaned by Citranox at 140 °F for 10 min followed by Almeco 18 at 140 °F for 10 min still had a tungsten oxide layer, however it is thinner than those cleaned by solvents and Detergent-8.

3. TZM Molybdenum

The spectra of samples cleaned by different cleaners were analyzed for carbon, oxygen and molybdenum by measuring the area of the corresponding peaks from survey spectra, and the results are shown in Figure 8. Once again, Almeco 18 and Citranox were more effective at removing carbon than solvents and Detergent-8, and the highest surface concentration of molybdenum was found on samples cleaned by Citranox. Analysis of low energy spectra also showed that Almeco 18 is the most effective at removing silicon.

Figure 9 shows Mo 3d spectra at ~230 eV. It can be seen that very weak Mo or molybdenum oxide peaks were found on samples cleaned by solvents. Samples cleaned by Almeco 18 and Detergent-8 show relatively thick molybdenum oxide layers. Of the cleaners tested, Citranox is the most effective at removing molybdenum oxides.

CONCLUSION

1. 304 stainless steel, machinable tungsten, and TZM molybdenum surfaces contain relatively thick layers of metal oxides and other contaminants after machining processes, such as cutting, milling, grinding, etc. The surface contamination cannot be effectively removed by solvents.

2. (a). Of the cleaners tested, the liquid alkaline cleaner Almeco 18 is the most effective at removing carbon-based organic contaminants and foreign particulates imbedded on the material surface by machining processes. The detergent can be used at ~140 °F with ultrasonic agitation for 15-20 min to clean the materials. It was found that Almeco 18 can also remove tungsten oxides, although it is not effective at removing other metal oxides, such as iron oxides and molybdenum oxides.

(b). The citric-acid-based cleaner Citranox was found to be very effective at removing metal oxides, such as iron oxides, molybdenum oxides, and tungsten oxides at mild temperatures with ultrasonic agitation. Cleaning temperature and time vary with the material to be cleaned. This detergent can replace strong inorganic acids to improve cleaning safety and minimize chemical waste disposal and other environmental problems.

(c). Of the cleaners tested, the liquid alkaline cleaner Detergent-8 is the least effective at removing organic and inorganic contaminants and metal oxides.

3. Almeco 18 and Citranox in a definite sequence may be used for in certain applications. This work requires further study.

Acknowledgement

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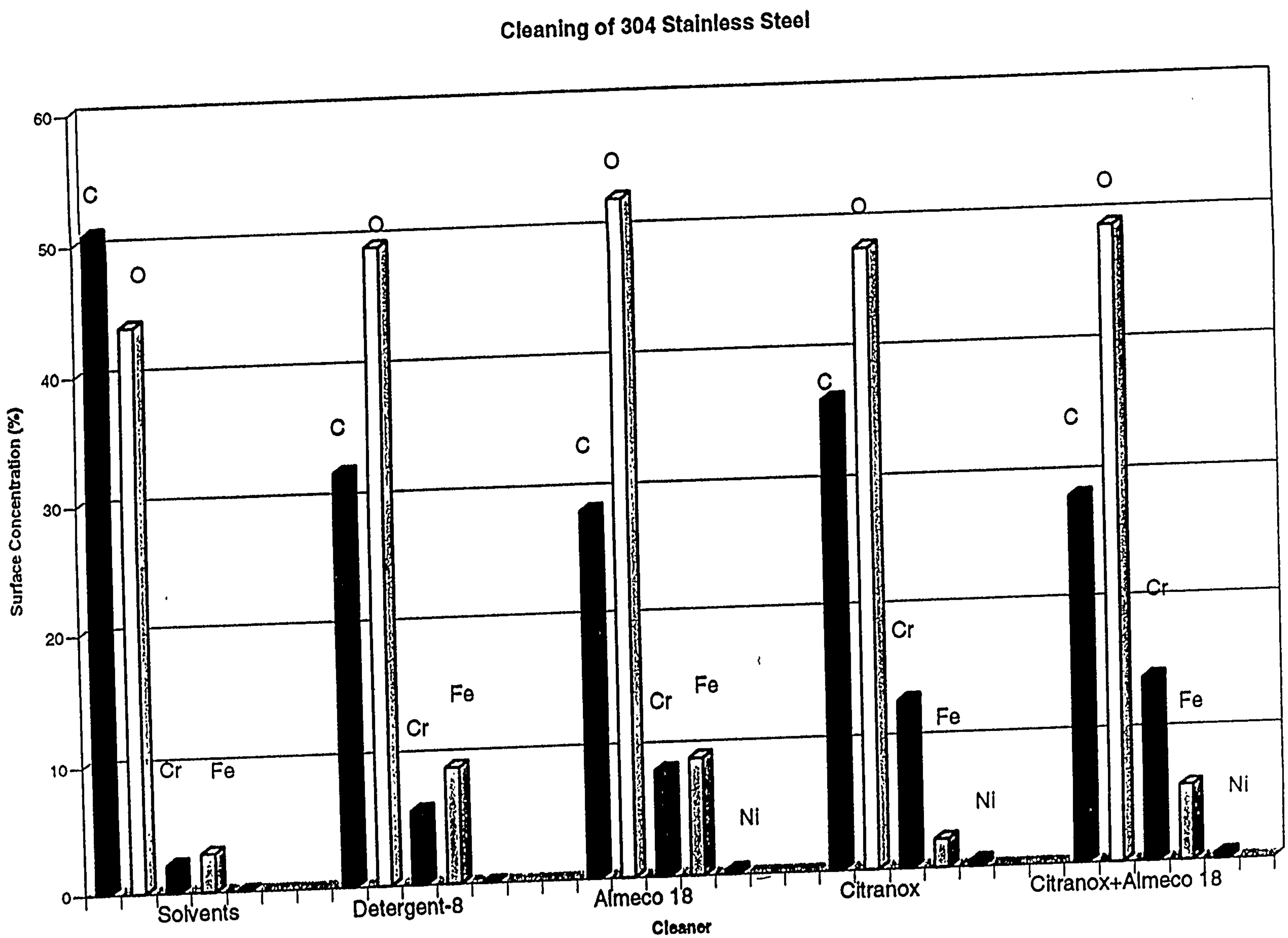

Figure 1. Carbon, oxygen, chromium, iron and nickel surface concentration (%) as determined by XPS of 304 stainless steel cleaned with different cleaners.

Fig. 1

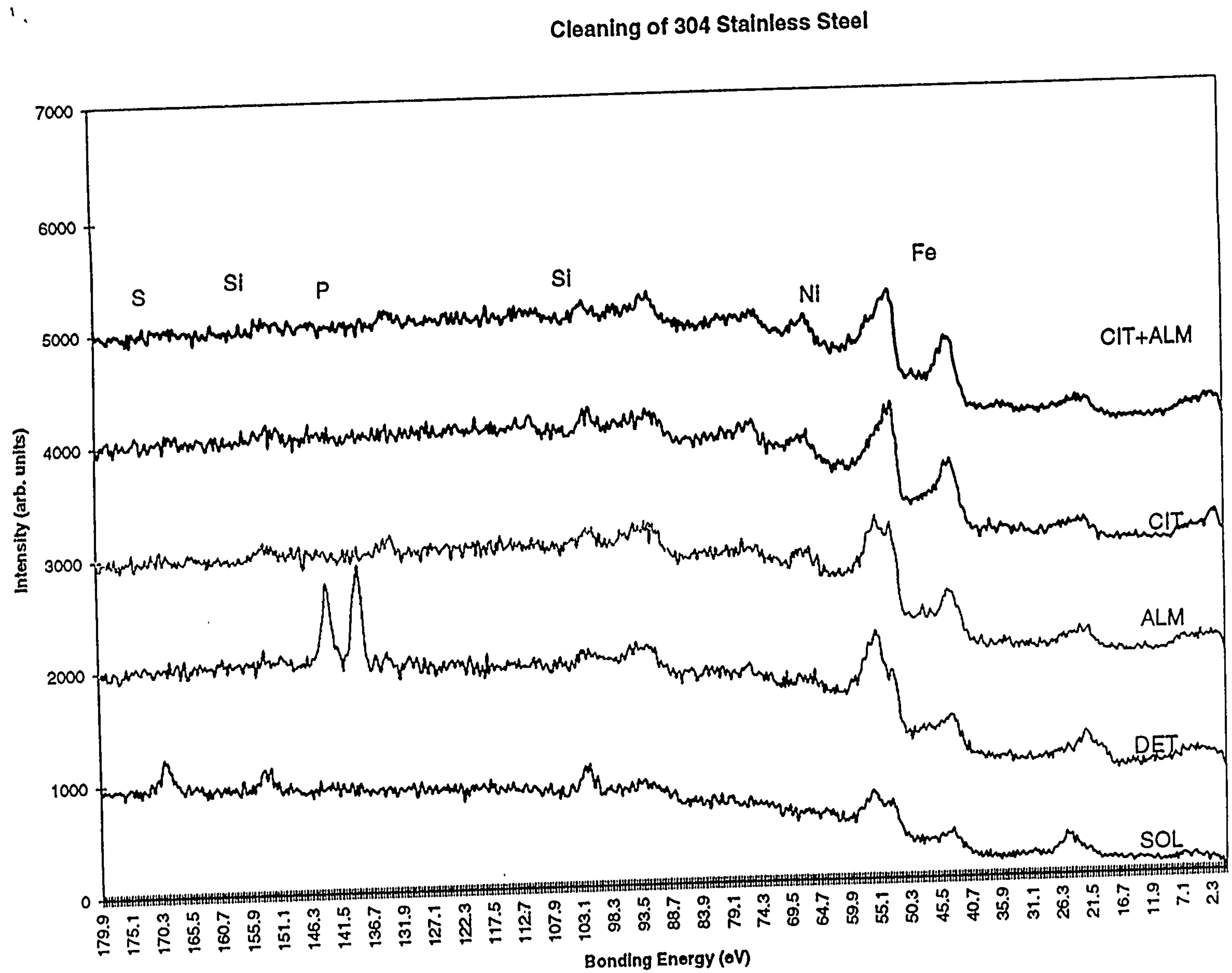

Figure 2. Low energy XPS spectra of 304 stainless steel cleaned with different cleaners. The spectra have been offset for clarity.

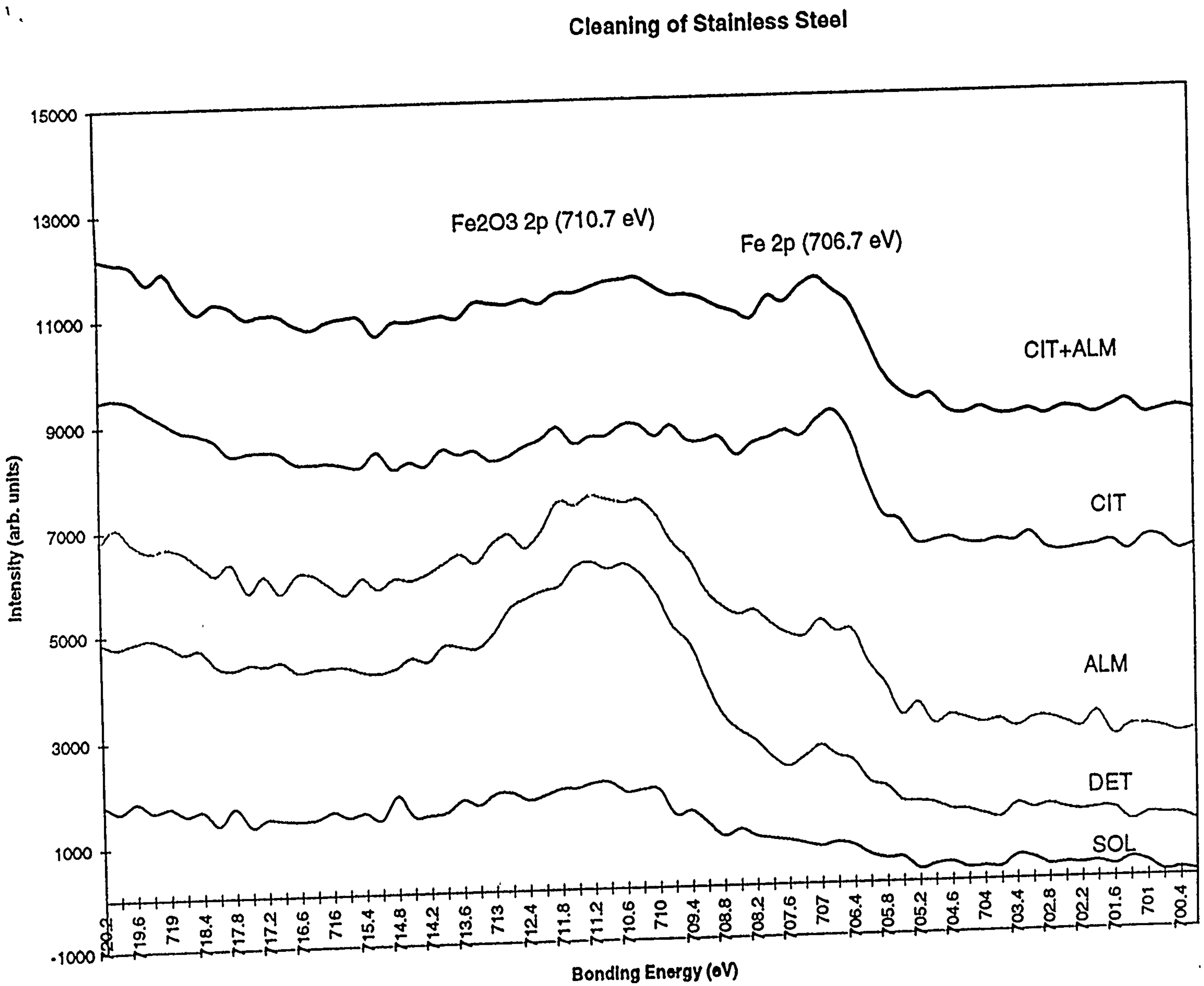

Figure 3. Iron 2p and iron oxide 2p XPS spectra of 304 stainless steel cleaned with different cleaners. The spectra have been offset for clarity.

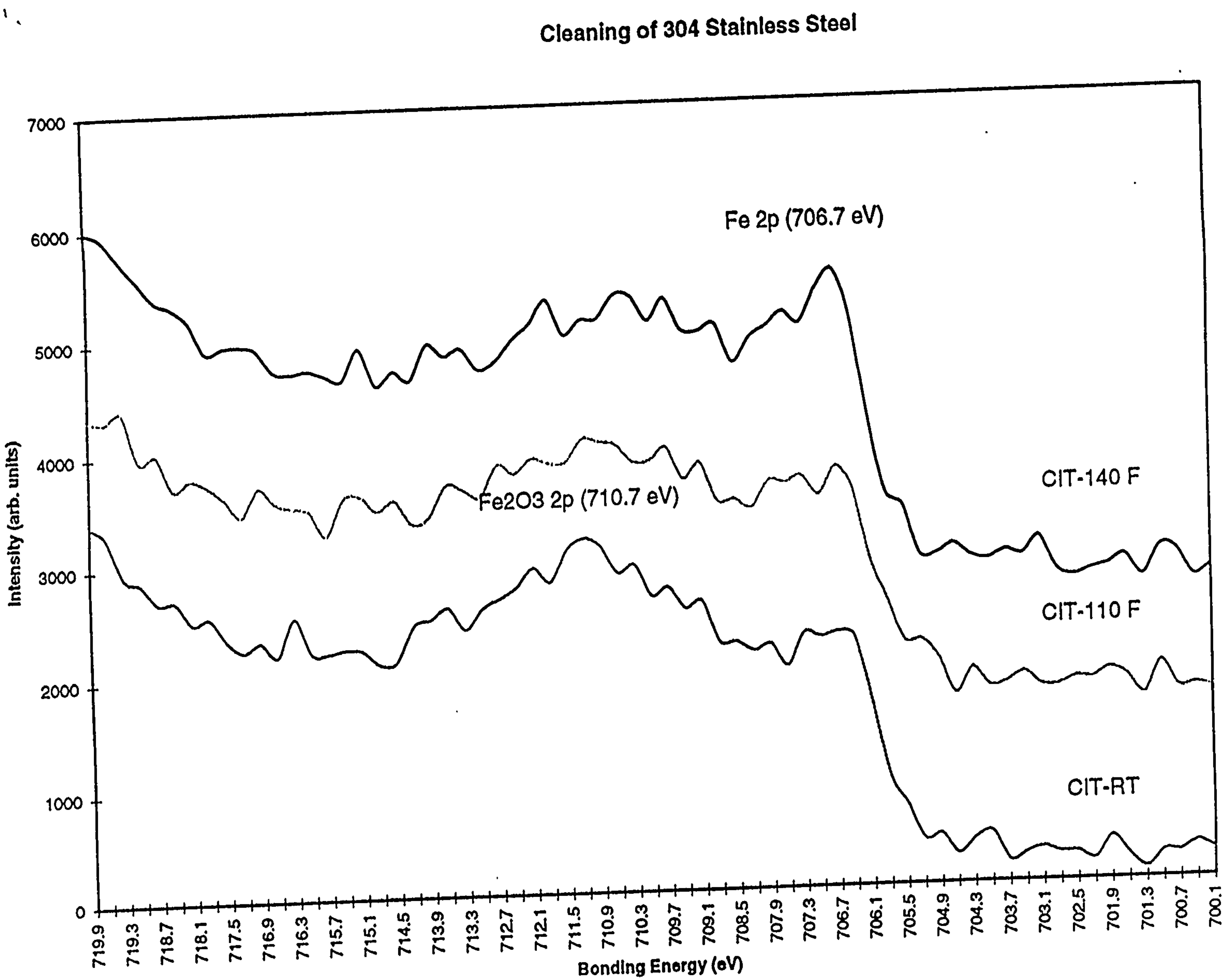

Figure 4. Iron 2p and iron oxide 2p XPS spectra of 304 stainless steel cleaned with Citranox at different temperature. The spectra have been offset for clarity.

Fig. 4

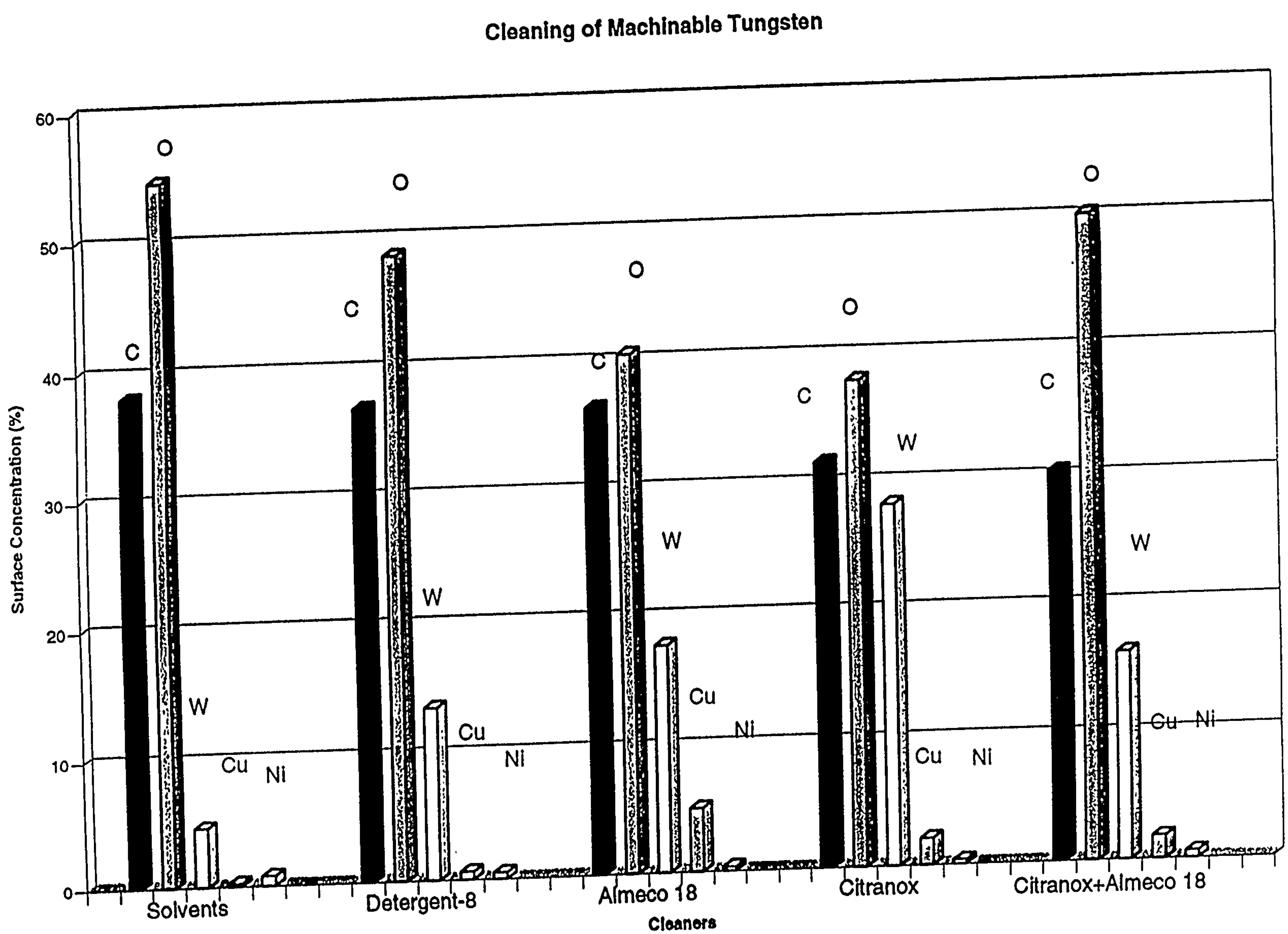

Figure 5. Carbon, oxygen, tungsten, copper and nickel surface concentration (%) as determined by XPS of machinable tungsten cleaned with different cleaners.

Fig. 5

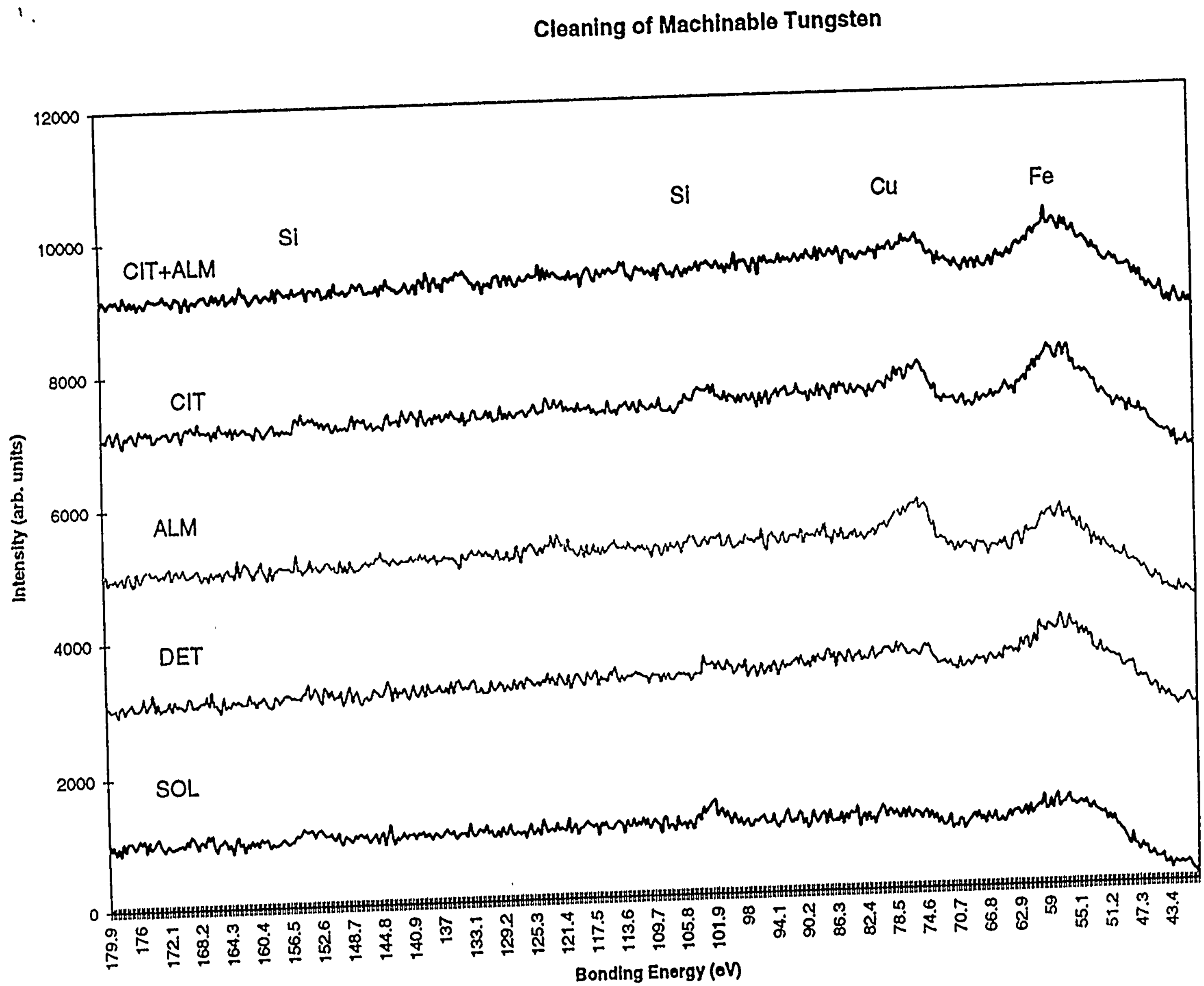

Figure 6. Low energy XPS spectra of machinable tungsten cleaned with different cleaners. The spectra have been offset for clarity.

Fig. 6

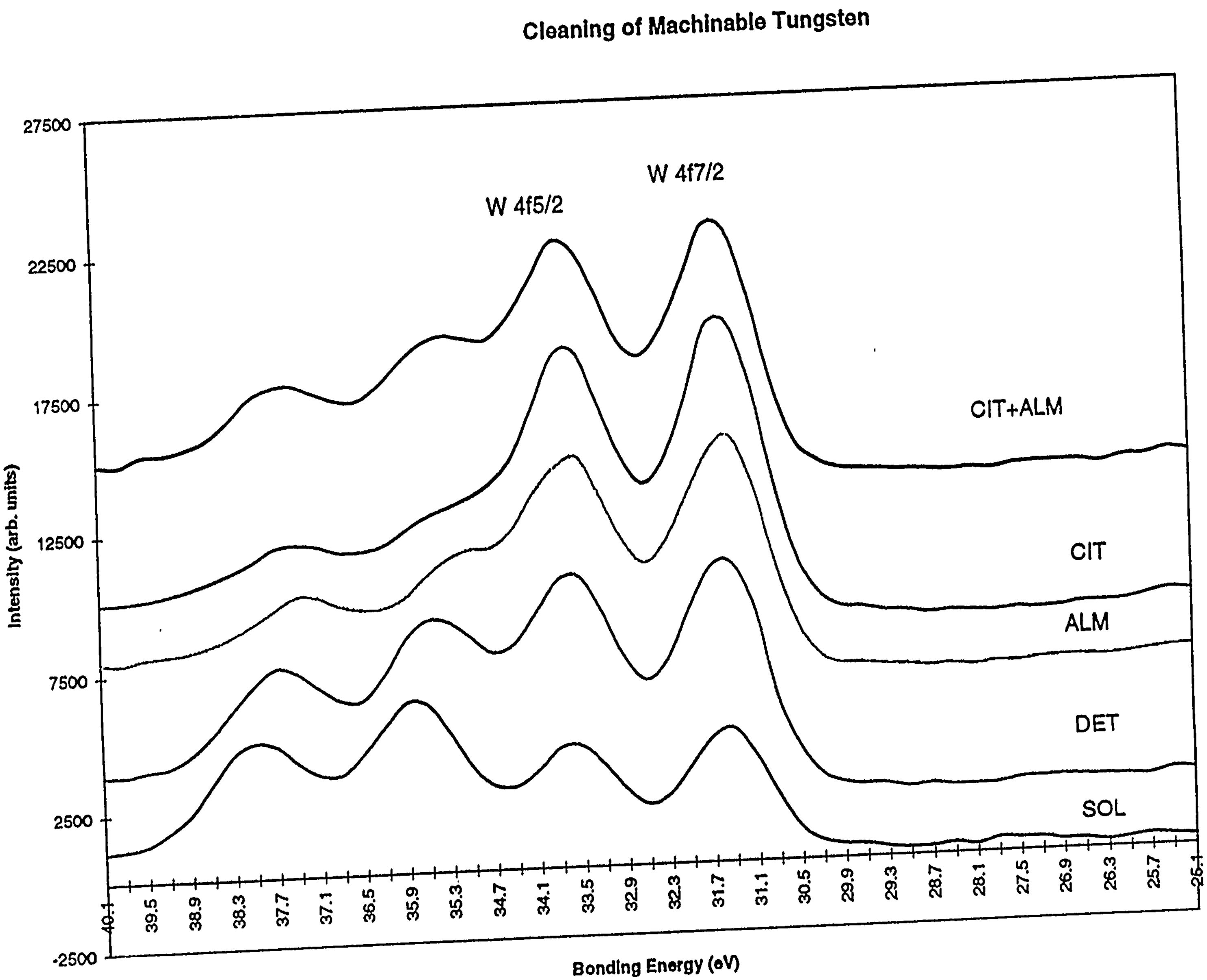

Figure 7. Tungsten 4f and tungsten oxides XPS spectra of machinable tungsten cleaned with different cleaners. The spectra have been offset for clarity.

Fig. 7

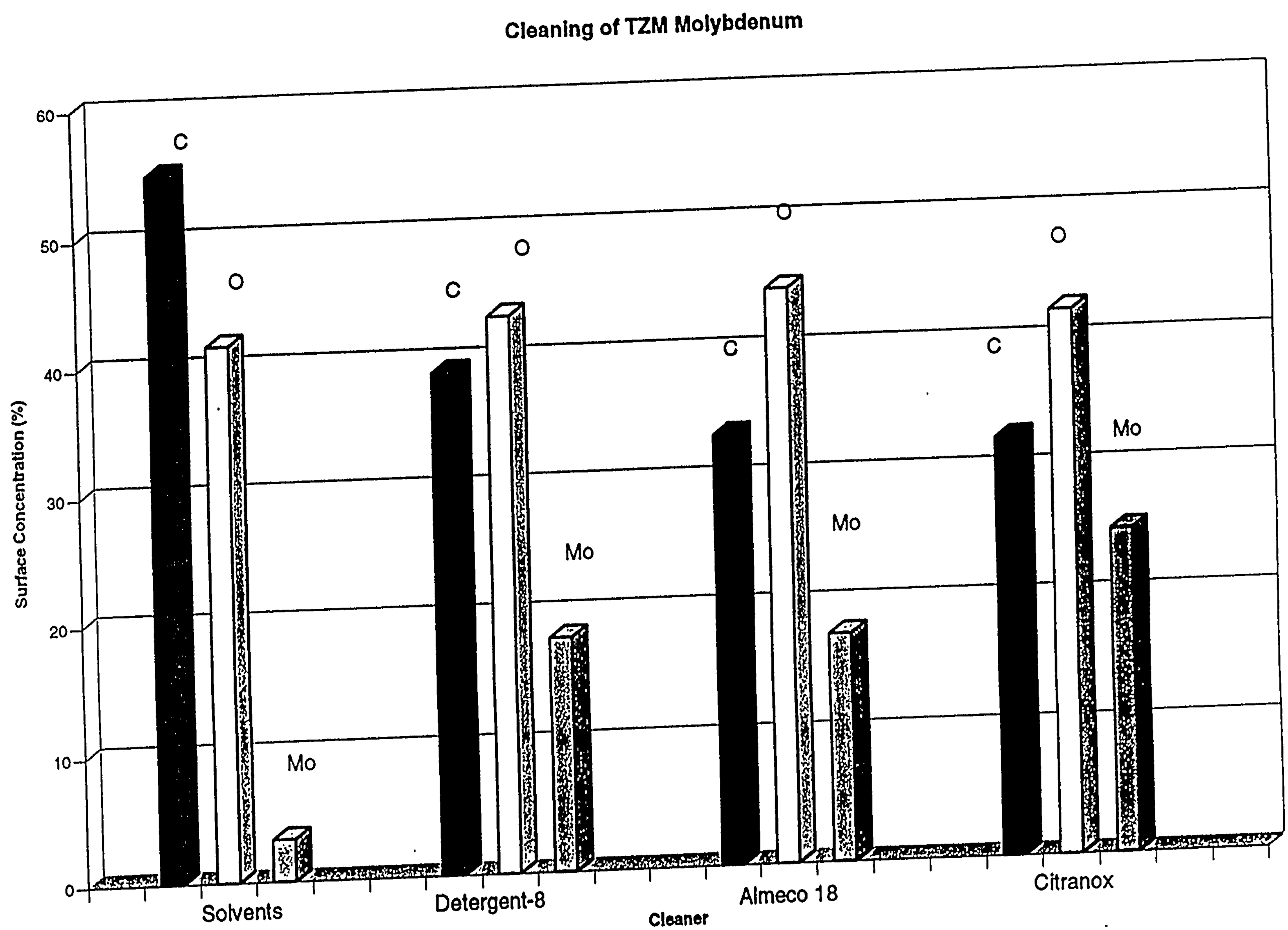

Figure 8. Carbon, oxygen, and molybdenum surface concentration (%) as determined by XPS of TZM molybdenum cleaned with different cleaners.

Fig. 8

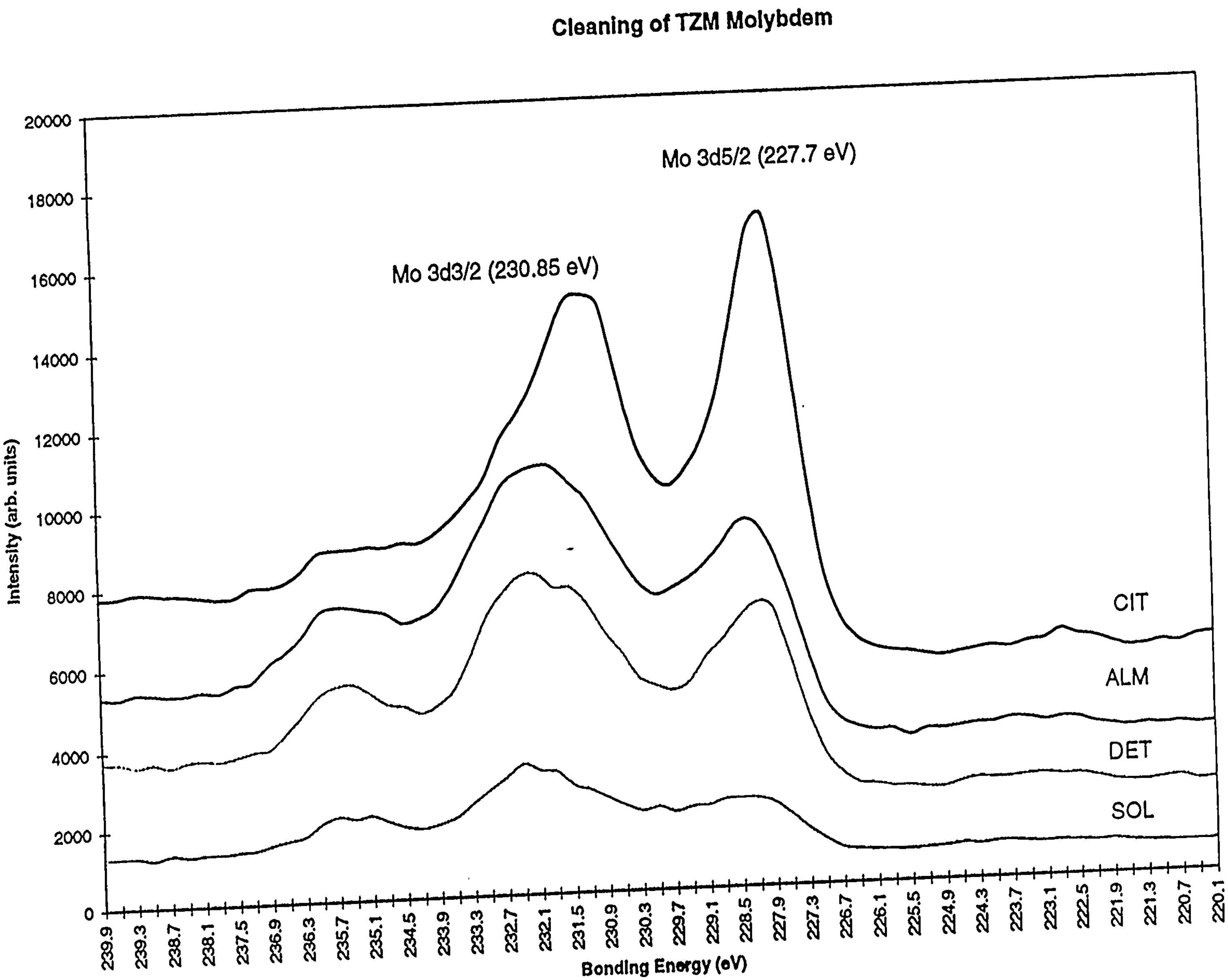

Figure 9. Molybdenum 3d and molybdenum oxide XPS spectra of TZM molybdenum cleaned with different cleaners. The spectra have been offset for clarity.

Fig. 9