Microscopy AND
Microanalysis

Reinvestigation of the M Emission Spectrum of Uranium-92

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Abstract: The M spectrum of the element uranium was reinvestigated by using both high-resolution wavelength dispersive (WD) spectrometry as well as energy dispersive (ED) spectrometry. Thereby we observed relative intensities that deviate from data in the literature. These discrepancies were not only observed for the weak U M lines but also for major lines. By measuring the Mα,β region of the spectrum with a PET crystal in second-order reflection, a sufficient energy resolution was achieved to separate Mα_2 (M_5N_6) from Mα_1 (M_5N_7). The intensity ratio $I(M_5N_6)/I(M_5N_7)$ was determined to be approximately 5%, which is in strong contrast to the data tabulated by White and Johnson [White, E.W. & Johnson, G.G. (1970). *X-Ray and Absorption Wavelengths and Two-Theta Tables*. ASTM Data Series DS37A, 2nd ed. Philadelphia, PA: American Society for Testing and Materials]. Furthermore M_5N_7 was clearly observed as the strongest of the M lines that disagrees with data presented by Kleykamp [Kleykamp, H. (1981). Wavelengths of the M X-ray spectra of uranium, neptunium, plutonium, and americium. *Z Naturforsch* **36a**, 1388–1390], who reported Mβ (M_4N_6) as the strongest line. Also, after White and Johnson (1970), the line M_2N_4 should be more intense than M_3O_5 by a factor of 5. Both our WD and ED spectra show clearly that M_3O_5 is stronger than M_2N_4. Altogether, we observed in our WD spectra 26 M lines. In some cases untypical large differences between the line energies given by Bearden [Bearden, J.A. (1967). X-ray wavelengths. *Rev Mod Phys* **39**, 78–124] and measured by us were observed.

Key words: X-ray spectrometry, electron microprobe analysis, wavelength dispersive spectrometry, silicon drift detector (SDD), uranium, M emission spectrum, relative intensities

INTRODUCTION

The first report on the observation of M emission lines was presented by Siegbahn (1916). He investigated the M radiation emitted by the elements [79]Au, [81]Tl, [82]Pb, [83]Bi, [90]Th, and [92]U. For each of these elements, he tabulated at least four M lines. For these measurements he used his first vacuum spectrometer with a gypsum crystal as the dispersing element. The radiation was detected by means of photographic plates. The wavelength values, λ, which he tabulated are in remarkable agreement with those tabulated by Bearden (1967). For example, the wavelength of U Mβ (M_4N_6) tabulated by Siegbahn is 3.715 Å, whereas Bearden has given for the same line a value of 3.716 Å. Furthermore, Siegbahn showed that for the α and β lines of the investigated elements a Moseley law is valid. Additionally, he assumed that the strongest of the M lines, α, consists of a triplet, but he was not able to resolve it.

Later, Siegbahn (1931) carried out more detailed investigations of the M emission spectra together with a number of PhD students. In his excellent monograph he wrote that the most detailed and accurate investigation of the M spectra was carried out by Lindberg (1928). In his 1928 article, Lindberg tabulated 18 M lines for [92]U. He was able to resolve the Mα triplet assumed by Siegbahn into its components α_2 (M_5N_6) at the low energy side of α_1 (M_5N_7) and a

satellite line α' (SMα) at the high energy side of α_1. Additionally, he observed α_1 (M_5N_7) as the strongest of the U M lines, followed by β (M_4N_6), whereas α_2 (M_5N_6) was observed as a rather weak line.

This observation would qualitatively agree with the intensity rules for this group of lines that were given by Lindberg (1928) as $I(M_5N_7):I(M_4N_6):I(M_5N_6) = 20:14:1 = 100:70:5$.

In his classical compilation Bearden (1967) tabulated 19 M lines for [92]U. In the second edition of the *Handbook of X-Ray Data*, Zschornack (2007) tabulated 26 M lines for the same element. This was achieved mainly by including the data presented by Cauchois and Senemaud (1978). Unfortunately, neither Bearden nor Cauchois and Senemaud gave data for the relative intensities (RI). Thus, with respect to those data we are limited to the ASTM tables prepared by White and Johnson (1970) and to some data published by Kleykamp (1981). The data given by these authors are quite different not only for the weak M lines of [92]U but also for the strong lines α_1 (M_5N_7), α_2 (M_5N_6), and β (M_4N_6). After White and Johnson, α_2 has the same RI as α_1, namely 100%. In contrast to this information, Kleykamp observed α_2 as too weak in intensity for a precise energy determination. The next problem relates to β (M_4N_6). White and Johnson tabulated the RI of this line as 60% but Kleykamp gave a RI of 180%. Concerning these discrepancies, a more recent article dealing with the electron probe microanalysis of actinide elements provided no clarifying details (Walker,

1998). The large differences between the relative intensities of the different authors were one of the main reasons for us to reinvestigate the uranium M spectrum.

The U M spectrum is very broad, ranging from 2.455 keV at the low energy end up to 5.524 keV at the high energy end. To take a full wavelength dispersive (WD) spectrum using the PET crystal of our microprobe the L-value (L is the distance from the X-ray source to the reflecting crystal) must be changed from about 70 mm up to about 170 mm. This change is connected with a strong reduction of the accepted solid angle. For more details the reader is referred to the monograph written by Reed (1993, p. 75). Therefore, relative intensities of such broad spectra should not be determined on the basis of relative net peak heights (RNPH). The strong dependence on the accepted solid angle can be effectively reduced if peak-to-background ratios (PBR) are used to deduce the relative intensities.

Materials and Methods

The measurements were carried out using a JXA 8800 L microprobe (JEOL Ltd., Tokyo, Japan). The take-off angle of this instrument is 40°. The energy of the exciting electrons, E_0, was in most cases 20 keV. Spectra were taken using both WD spectrometry and energy dispersive (ED) spectrometry. The ED spectra were taken with a SD detector X Flash 4010 (Bruker Nano GmbH, Berlin, Germany), specified with a full-width at half-maximum (FWHM) of $\leq$125 eV for Mn Kα and $\leq$47 eV for C Kα.

Most of the WD spectra were taken with a PET crystal with $2d = 8.742$ Å as the dispersing element. But the high-energy part of the U M spectrum was measured also with a LiF crystal with $2d = 4.0267$ Å. If these crystals are used, the X-rays in our microprobe are detected by means of a sealed Xe-filled proportional counter (XPC).

Generally, all WD spectra were taken in the differential pulse height analysis mode. The voltage of the proportional counter and the gain of the pulse amplifier were selected in such a manner that the mean pulse height of the uranium Mα quanta was 4 V. For spectra taken in first-order reflection, the lower level of the discriminator was set to 2 V and the window width to 4 V.

When studying the M emission spectrum of ^{68}Er, we have shown that an improved energy resolution can be achieved by recording the spectra in second-order reflection (Dellith & Wendt, 2007). Therefore, the central part of the U M spectrum around Mα, β was also measured with a PET crystal in second-order reflection with optimized discriminator settings as described in Dellith and Wendt (2007).

To find out the reason for the unusual observation of Kleykamp (1981) that the β line of uranium is nearly two times higher than the α line, we have also taken the central part of the M spectrum around Mα, β in second- and fourth-order reflection using a TAP crystal with $2d = 25.757$ Å. In that case the X-rays are detected in our microprobe by means of a gas flow proportional counter (GPC) operating with P10 counting gas (90% argon, 10% methane).
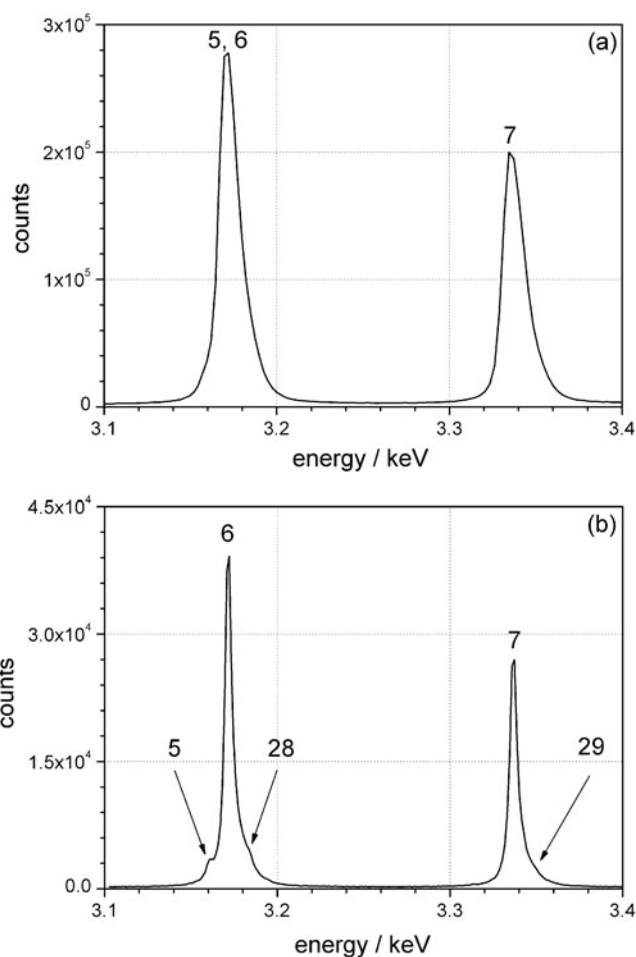

Figure 1. Central part of the U M spectrum taken in (**a**) first-order and (**b**) second-order reflection. The energy resolution of the spectrometer in panel **b** is greatly improved and enables the separation of Mα_2 (5) from Mα_1 (6).

Originally, a polished uranium metal was used as U standard. The sample was delivered by JEOL Ltd. a number of years ago. Obviously U has a rather strong tendency to oxidize, which seems to be typical for most metals. By grinding the sample immediately before the measurement, we were able to reduce the O Kα intensity strongly but not completely.

Results and Discussion

The results of our search for U M peaks are summarized in Table 1. With the exception of the peaks No. 5 (M$_5$N$_6$, α_2), No. 6 (M$_5$N$_7$, α_1), No. 28 (satellite line SMα_1), and No. 29 (satellite line SMβ), all peaks were observed when using first-order reflection.

In the last column of Table 1, our results of the relative intensities are given. These data were derived from a full spectrum taken in first-order reflection using the PET crystal at $E_0 = 20$ keV. Figures 1a and 3 are parts of this spectrum. As written in the introduction, the relative intensities were determined on the basis of the PBR, not on the basis of the RNPH values. The difference will be illustrated by an

Table 1.   Correlation between the Numbers Given in the X-Ray Spectra and the Observed X-Ray Lines.

| No. | Transition | Position from Reference (eV) | | | | | Relative Intensity This Work (%) |
		Bearden (1967)	Lindberg (1928)	Cauchois et al. (1978)	Kleykamp (1981)	This Work	
1	M_4N_2 (ζ_2)	2,455	2,455	2,455	2,456	2,455	1.7
2	M_5N_3 (ζ_1)	2,507	2,506		2,503	2,507	2.3
3	M_4N_3	2,681	2,681			2,683	0.2
4	M_3N_1	2,863	2,863	2,859	2,863	2,862	1.3
5	M_5N_6 (α_2)	3,160	3,161	3,162		3,162	100
6	M_5N_7 (α_1)	3,171	3,171	3,172	3,171	3,171	
7	M_4N_6 (β)	3,337	3,336	3,336	3,336	3,337	60
8	M_4O_2	3,467	3,466	3,468	3,467	3,468	0.4
9	M_3N_4	3,521	3,521	3,522	3,522	3,522	0.7
10	M_4O_3			3,531		n. obs.[a]	—
11	M_3N_5 (γ)	3,563	3,563	3,564	3,564	3,562	6
12	$M_4P_{2,3}$			3,698		3,697	0.2
13	M_2N_1	3,724	3,725		3,722	3,726	0.9
14	M_3N_7			3,920		3,922	0.1
15	M_3O_1	3,980	3,973	3,978		3,981	0.3
16	M_3O_4			4,200		n. obs.	—
17	M_3O_5	4,205	4,206	4,206	4,201	4,206	1.5
18	M_3P_1			4,231		4,231	0.2
19	M_1N_2	4,250		4,274	4,265	4,277	0.4
20	M_2N_4	4,401	4,397	4,400	4,398	4,402	0.6
21	M_1N_3	4,500	4,508	4,506	4,502	4,503	0.1
22	M_2O_1			4,844		4,864	0.03
23	M_2O_4	5,075	5,072			5,078	0.2
24	M_2P_1			5,119		n. obs.	—
25	M_1O_2					5,288	0.03
26	M_1O_3	5,380		5,382		5,353	0.2
27	M_1P_3	5,500				5,524	0.03
28	$SM\alpha_1$[b]		3,184			3,184	
29	$SM\beta$[b]		3,346			3,348	

[a]n. obs. = not observable.

[b]Regarding the satellite lines Cauchois and Senemaud (1978) tabulated three satellites of α_1 M_5N_7, three satellites of β M_4N_6, and one satellite of γ M_3N_5. We were not able to observe these satellite lines in our spectra.

example. The line with the highest PBR is the unresolved α line (5,6) with a PBR of approximately 120. In its maximum it contains 275,000 counts. The PBR of the ζ_1 line (2), shown in Figure 3, is approximately 2.8. The net peak height of this line contains 2,200 counts. Thus, the relative intensity $I(\zeta_1)/I(\alpha)$ derived from the RNPH values would be only 0.8%, whereas that derived from the PBR values is approximately 2.3%.

The central part of the uranium M spectrum taken at $E_0 = 20$ keV using (a) first-order and (b) second-order reflection is shown in Figure 1. In both cases the PET crystal was used together with a XPC. In the first-order spectrum, the FWHM of the α line (consisting of the peaks Nos. 5, 6, and 28) was determined to approximately 13 eV. As one can see, the peaks appear much sharper in the second-order spectrum. Here, the FWHM of the α_1 line M_5N_7 was determined to approximately 5.5 eV. As a consequence of this strongly improved energy resolution, the line Nos. 5, 28, and 29 become visible, at least as partially resolved shoulders. From Figure 1b the relative net peak height ratio (RNPHR) of $\beta/\alpha_1 \equiv M_4N_6/M_5N_7$ was determined to approx-

imately 70%. Due to the overlap between peak Nos. 5 and 6, the RNPHR of $\alpha_2/\alpha_1 \equiv M_5N_6/M_5N_7$ can only roughly be estimated to be approximately 5%. On the one hand, these observations strongly support the intensity rules published by Lindberg (1928). On the other hand, our result regarding the lines M_5N_6 and M_5N_7 is in a strong contrast to the data published by White and Johnson (1970).

The central part of the U M spectrum taken at $E_0 = 20$ keV is also shown in Figure 2. But this spectrum was taken in fourth-order reflection using a TAP crystal together with a GPC. Also shown in Figure 2 is an arrow that indicates the K absorption edge of the ^{18}Ar counting gas, which was given by Bearden and Burr (1967) at (3202.9 ± 0.3) eV. Thus, the U M_5N_7 line is of lower energy than the Ar K edge and will be absorbed much weaker than the U M_4N_6 line, which is of higher energy than the Ar K edge. In principle, the spectrum shown in Figure 2 is very similar to that shown by Kleykamp (1981). Therefore, we assume that Kleykamp used a P10 filled gas flow proportional counter for the X-ray detection. But unfortunately, in his article he did not give detailed information on the detection system.
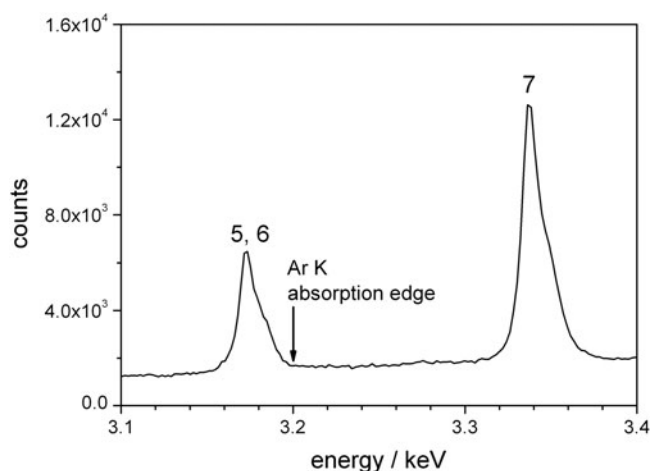
Figure 2. Central part of the U M spectrum taken in fourth-order reflection using a TAP crystal together with a GPC. Due to the position below the Ar K absorption edge, the detection efficiency of M$\alpha_{1,2}$ (5, 6) is reduced, and this line therefore appears much weaker than the M β line (7) with an energy above the Ar K edge.
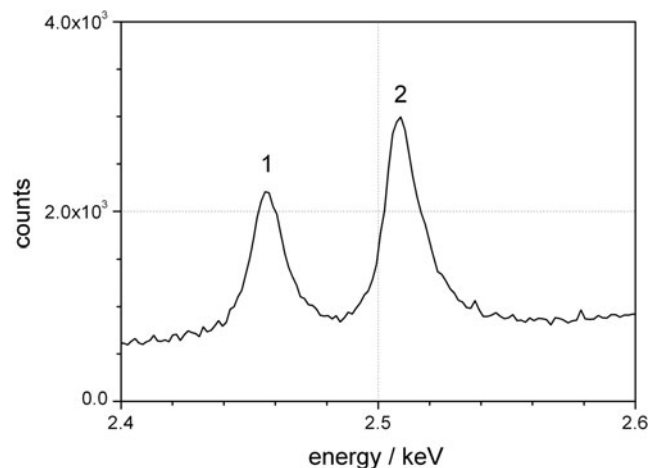

Figure 3. The low-energy lines Mζ_1 (2) and Mζ_2 (1) of the uranium M spectrum. The observed intensity ratio ζ_2/ζ_1 is in strong contrast to the value given by White and Johnson (1970).

A similar case is described in the monograph written by Goldstein et al. (2003). In Figure 8.20b of this work, a Cd L spectrum is shown versus the radiation energy. This spectrum was taken using a PET crystal together with an XPC. Here, the Cd Lα line at 3,134 eV (Bearden, 1967) is the strongest of the Cd L lines and about two times higher than the Cd Lβ_1 line at 3,317 eV. In Figure 8.23, a Cd L spectrum is shown that was also taken with a PET crystal but now together with a GPC operating with P10 gas. In that spectrum the Lβ_1 line is more intense than the Lα_1 line. Again, the energy of the Cd Lα_1 line is below the energy of the Ar K edge and therefore less absorbed than the Cd Lβ_1 line with an energy above the Ar K edge.

The two U M lines of lowest energy, M$_4$N$_2$ (ζ_2) and M$_5$N$_3$ (ζ_1), are shown in Figure 3. This part of the U M spectrum was taken using the PET crystal in first-order
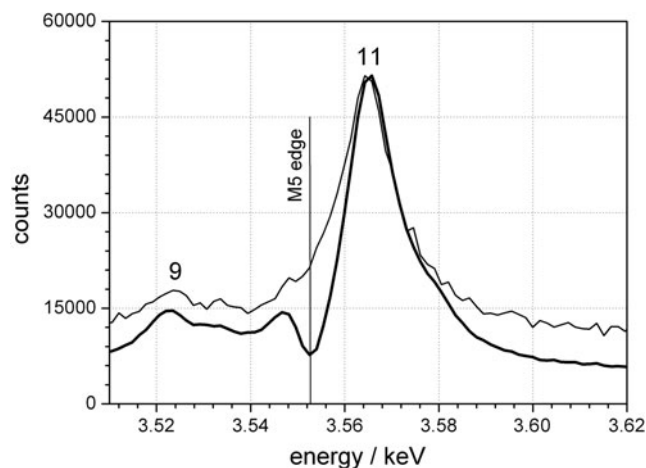

Figure 4. The U M lines Mγ (11) and M$_3$N$_4$ (9) taken at $E_0 = 7$ keV (thin) and $E_0 = 20$ keV (thick). The Mγ line is affected by the M$_5$ absorption structure of uranium.

reflection together with the sealed XPC. The net peak height ratio of the M$_4$N$_2$ line relative to that of the M$_5$N$_3$ line is approximately 70%, which is in strong contrast to the 10% given by White and Johnson (1970). The first of the heavy elements for which Bearden (1967) has given separate ζ lines is ^{72}Hf. For both, ζ_1 and ζ_2, he has given the same energy, 1,280 eV. From the binding energies tabulated in Bearden and Burr (1967), we have calculated $E(M_5N_3) = (1,281.3 \pm 0.9)$ eV and $E(M_4N_2) = (1,279.4 \pm 0.9)$ eV. In any case the lines are so close to each other that it would be rather difficult to resolve them. But in principle it is not completely correct to identify the ζ line of ^{68}Er only as M$_5$N$_3$ as done in Dellith and Wendt (2007) because this peak is an unresolvable doublet consisting of M$_5$N$_3$ and M$_4$N$_2$.

The high-energy range of the U M spectrum was measured in first-order reflection also by means of a LiF crystal, which has a slightly better resolution than the PET crystal. In Figure 4 the region around the γ line M$_3$N$_5$ is shown. The thicker drawn of the two spectra was taken at $E_0 = 20$ keV. Here, the γ line appears asymmetrically. Furthermore, a small peak is visible at approximately 3,547 eV. Both effects disappear in the thinner drawn spectrum, which was taken at $E_0 = 7$ keV. They are caused by the M$_5$ absorption edge of ^{92}U, which was given in Bearden and Burr (1967) at $(3,551.7 \pm 0.3)$ eV.

Another section of the high-energy range is shown in Figure 5. As one can see the M$_3$O$_5$ transition is somewhat more than two times higher than the M$_2$N$_4$ peak, which is in contrast to the data given by White and Johnson (1970). The background jump at nearly 4,780 eV is caused by the Xe L$_3$ absorption edge, which means that the detection efficiency of the Xe-filled proportional counter increases by approximately 30% if the X-ray energy exceeds the energy of the Xe L$_3$ absorption edge.

A full uranium M spectrum taken at $E_0 = 20$ keV with a silicon drift-chamber detector is shown in Figure 6a. To see the weak M lines more clearly, in Figure 6b the same
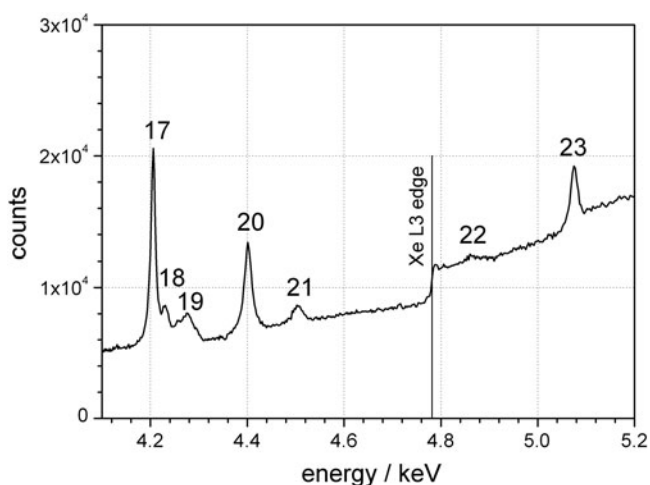
Figure 5. High-energy part of the U M spectrum taken with a LiF crystal. The background jump at nearly 4,780 eV is the Xe L3 absorption edge caused by the Xe-filled proportional counter.

spectrum is shown with an ordinate scale magnified by a factor of 10. From this spectrum the relative intensities were determined that are summarized in Table 2, where the data published by White and Johnson (1970) and Kleykamp (1981) are shown for comparison.

The rather strong peak at the lowest energy is the unresolved ζ line consisting of M_5N_3 and M_4N_2. By that reason its FWHM of 120 eV is larger than that of the neighboring M_3N_1 line with a FWHM of 95 eV.

The RNPHR of $\beta/\alpha \equiv (M_4N_6 + SM\beta)/(M_5N_7 + M_5N_6 + SM\alpha)$ is somewhat smaller than that of β/α_1 determined from Figure 1b and amounts approximately 60%. The reason for that slight variation is caused by the different performance of the ED and WD technique. As in the case of the WD spectrum shown in Figure 5, the M_3O_5 line is approximately two times higher than the M_2N_4 peak.

Table 2. Relative Net Peak Height Ratios of the U M Lines Deduced from the ED Spectrum Shown in Figure 6 in Comparison with the Data Published by White and Johnson (1970) and Kleykamp (1981).

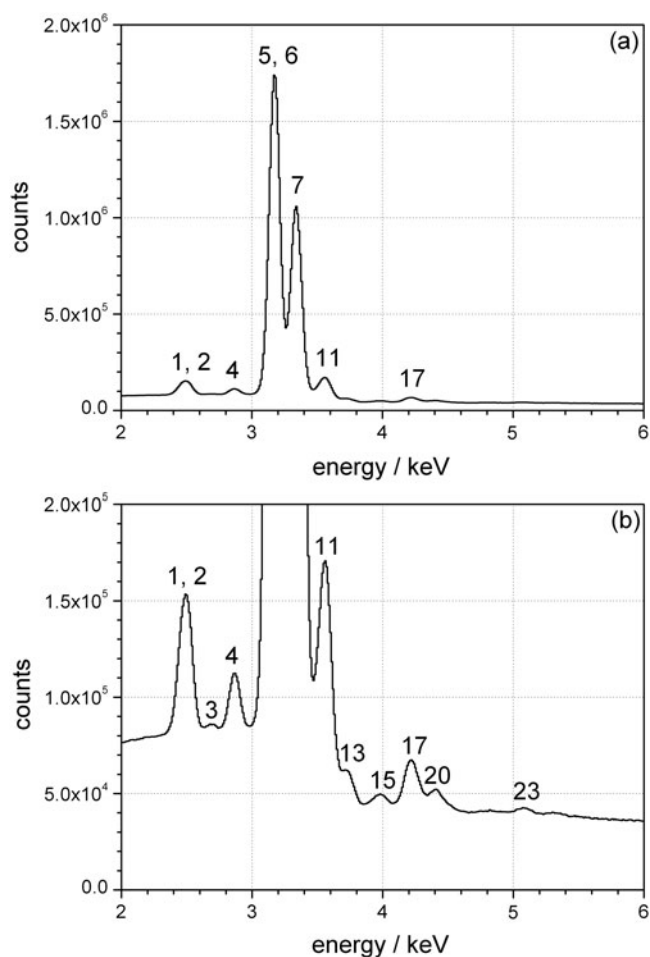| No. | Line | Relative Intensity (%) | | |
		White and Johnson (1970)	Kleykamp (1981)	This Work
1,2	$\zeta_{1,2}$	1.1	1.5	4
3	M_4N_3	0.01	—	0.15
4	M_3N_1	1	0.5	1.5
5,6	$\alpha_{1,2}$	200	100	100
7	β	60	180	60
11	γ	5	13	7
13	M_2N_1	0.01	1	1
15	M_3O_1	0.5	—	0.4
17	M_3O_5	1	5	1.5
20	M_2N_4	5	2	0.7
23	M_2O_4	0.01	—	0.2

Figure 6. ED M spectrum of uranium taken at $E_0 = 20$ keV with a silicon drift detector. In total 11 M lines are observable. In relation to panel **a**, the ordinate scale in panel **b** is magnified by a factor of 10.

In comparison with WD spectrometry, the energy resolution of ED spectrometry is worse by roughly one order of magnitude. Therefore, the detection sensitivity of ED spectrometry is much lower than that of WD spectrometry, which results in a much lower number of uranium M lines that could be doubtless identified in the ED spectrum shown in Figure 6.

Conclusions

Finally, one can conclude that the very early articles, in particular that presented by Lindberg (1928), provided reliable data about the uranium M spectrum. Even the relative intensities, expressed by Lindberg in the intensity rules, are in a remarkable agreement with the results of the present work. Otherwise, our observations are partially in strong contrast with the data published by other authors many years later. For some of these discrepancies an explanation could be given.

In his original article from 1928, Lindberg had given the intensity rules discussed in the introduction of the present article without any reference to the method of how

he achieved these results. But some years later he published a review article about the M series (Lindberg, 1931), in which he explained that he deduced the intensity rules from the Burger-Dorgelo calculation (Burger & Dorgelo, 1924). A short but instructive example of such a calculation was given by Reed (1993, p. 300) in his monograph.

In energy dispersive spectrometry the accepted solid angle does not depend on the energy of the radiation. In contrast to that, in WD spectrometry the accepted solid angle decreases with increasing wavelength. To reduce this effect we have proposed in this article to deduce the relative intensities of broad WD spectra not from the measured net peak heights but from the peak-to-background ratios. In this manner the data in the last column of Table 1 were obtained. They are in remarkable agreement with the data deduced from the ED spectrum shown in Figure 6 and given in the last column of Table 2. This procedure is possible in the case of the U M spectrum because this spectrum is not affected by anomalous line-type absorption.

The knowledge of the weak M lines may be important if the purity of a U-containing sample has to be analyzed. The software of our microprobe does not contain the line M_1N_3. Therefore, this line is automatically misidentified as Ti Kα in the so-called A-rank, which means that this element is present without doubt. Furthermore, the software of the microprobe does not find the line M_1N_2 because the energy of this line given by Bearden deviates from the true one by approximately 25 eV.

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