

Identification of components in prosthetic alloys by X — ray emission spectroscopy

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Summary

The authors analysed the components of certain prosthetic alloys to determine their precise composition and to examine the possibilities of their applications. X-ray spectroscopy was used for analysis. Conclusions were made about the concentrations and make-up of components in the sample on the basis of variations in height and distribution of peaks. The method, therefore, is qualitative and quantitative and can be used with a minimal number of samples. The sample is not destroyed in analysis. This method is important in the field of fixed prosthodontics.

Key words: prosthetic alloys, composition, identification

Knowledge of the composition of prosthetic alloys is a necessary prerequisite for evaluating the changes that occur in the metal during processing, and also later within the organism. It is not possible to carry out an accurate analysis of changes in the quality and properties of metals without first being able to identify their composition before and after laboratory processing.

Scientists therefore have attempted with the aid of modern research techniques to gain insight into the qualitative and quantitative composition of dental alloys. Such alloys are appearing on the market in increasing numbers while their composition unfortunately is becoming more and more a trade secret. International standards and specifications such as DIN, ISO, FDI, ADA etc. do exist of course and serve to prevent hazardous products from appearing on the market. They are however, of little assistance in keeping the profession effectively informed about dental materials and especially about their behaviour during processing and within the organism. There are well known cases of uranium being discovered subsequently in certain porcelains and beryllium in some dental alloys, etc. Rarely a manufacturer will publish the composition of his product in full, as was the case with the American alloy for metallic ceramics, UNIBOND-UTK, which ADA accepted as a patented composition. For this reason various authors have used a number of methods in their investigations, such as activation ana-

lysis (Nally¹ 1968) atomic absorption spectroscopy (Trifunović³ 1981) and electrochemical procedures such as polarography, chromatography and related techniques.

This paper reports some of our investigations on the qualitative and quantitative analysis of dental alloys. We used X-ray emission spectroscopy which has been increasingly popular for analytical purposes over the last decade (Valković)⁶

MATERIALS AND METHODS

The materials under investigation consisted of a large number of domestic, foreign and experimental alloys for dental prostheses.

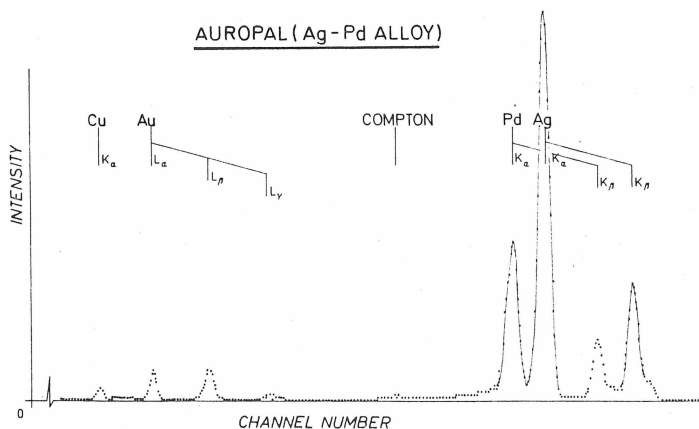
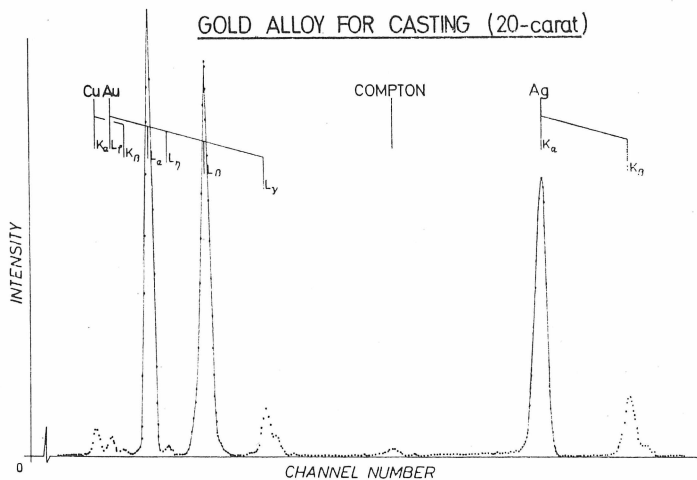
The samples were analysed with X-ray emission spectroscopy in the laboratories of the Ruđer Bošković Institute in Zagreb.

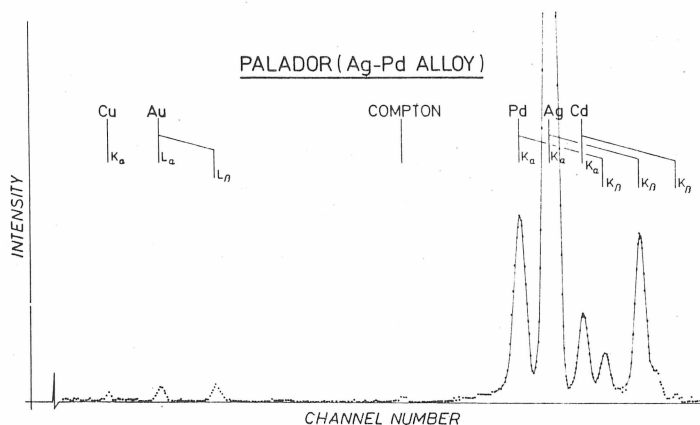
Periodic system of the elements

Atomic number	Symbol	Atomic number	Symbol	Atomic number	Symbol	Atomic number	Symbol
1	H	24	Cr	47	Ag	70	Yb
2	He	25	Mn	48	Cd	71	Lu
3	Li	26	Fe	49	In	72	Hf
4	Be	27	Co	50	Sn	73	Ta
5	B	28	Ni	51	Sb	74	W
6	C	29	Cu	52	Te	75	Re
7	N	30	Zn	53	I	76	Os
8	O	31	Ga	54	Xe	77	Ir
9	F	32	Ge	55	Cs	78	Pt
10	Ne	33	As	56	Ba	79	Au
11	Na	34	Se	57	La	80	Hg
12	Mg	35	Br	58	Ce	81	Tl
13	Al	36	Kr	59	Pr	82	Pb
14	Si	37	Rb	60	Nd	83	Bi
15	P	38	Sr	61	Pm	84	Po
16	S	39	Y	62	Sm	85	At
17	Cl	40	Zr	63	Fu	86	Rn
18	Ar	41	Nb	64	Gd	87	Fr
19	K	42	Mo	65	Tb	88	Ra
20	Ca	43	Tc	66	Dy	89	Ac
21	Sc	44	Ru	67	Ho	90	Th
22	Ti	45	Rh	68	Er	91	Pa
23	V	46	Pd	69	Tm	92	U

Fig 1 is a schematic illustration of the basic principle of this method. The sample is exposed to ionizing radiation from an X-ray tube which we used, accelerator and radioactive source. Ionization of atoms (ejection of electrons) in the

sample which results in the emission of characteristic X-ray occurs on exposure to radiation. The X-ray emitted by various elements can be distinguished by their different energies, i.e. wavelengths. The X-rays are detected with an appropriated detector (e.g. Si(Li)) and they are then sorted and counted with the aid of an analyzer. The energy of the X-rays allows elements to be identified whereas the line intensity in the X-ray spectrum can be registered by meanm of a chart recorder, enables the determination of concentrations of elements within the sample.





The apparatus can distinguish between K X-ray neighbouring elements heavier than sodium atomic number 11 and up to uranium with an atomic number of 92. This means that the following elements cannot be detected within the sample: H, He, Li, Be, B, C, N, O, F, Ne and Mg, whereas all other elements can be detected and their concentrations determined.

Table 1. Some samples of dental alloys examined by the method

	24	26	27	28	29	30	46	47	48	49	79	%							
	Cr	Fe	Co	Ni	Cu	Zn	Pd	Ag	Cd	In	Au								
yu gold alloys	old plate 22 carat												3,2	0,2	2,2	94,4	100		
	gold alloy for casting 20 carat												4,5	0,6	0,1	5,5	89,3	100	
	gold alloy for soldering 20 carat												7,9	1,6	0,3	0,9	3,9	85,3	100
yu Ag-Pd alloys	Palador												5,3	1,2	11,2	67,0	4,7	10,6	100
	Auroopal												12,6	1,6	15,2	59,9	10,7	100	
alloys for ceramic-metal prosthodontics	Degudent »U«												0,6	1,9	0,6	1,1	95,8	100	
	Wiron »S«												16,9	0,4	82,7	100			
	Ultratek												12,5	0,2	0,3	87,0	100		

RESULTS

The results and their ranges are shown in the tables.

Table 1 gives the percentages on the surface of eight selected dental alloys. These results were obtained on the basis of the following eight spectra.

Table 2. Some samples of gold alloys, yu-production (parts pér 100)

	gold plates			alloys for casting			alloys for soldering		
	22 carat A	22 carat B	22 carat C	20 carat A	18 carat A ₁	20 carat C	20 carat A	18 carat A ₁	16 carat A ₂
Au	94,4	93,6	94,7	89,3	79,7	89,5	85,3	78,3	71,8
Ag	2,2	2,5	2,3	5,5	4,5	6,1	0,3	2,5	3,4
Cu	3,2	3,3	2,6	4,5	15,0	3,9	7,9	13,0	17,9
Zn		0,3		0,6	0,7	0,5	1,6	1,2	2,1
Cd							3,9	4,8	4,8
Pd	0,2	0,3	0,4	0,1	0,1		0,3	0,1	0,1

Table 3. Some samples of Ag-Pd alloys (parts pér 100)

	alloys for casting				plates		
	Auropal	Palador	Palliag	Arpal	Auropal	Palador	Stomaor
Ag	59,9	67,0	51,5	44,2	66,2	72,3	69,0
Pd	15,2	11,2	18,4	11,6	18,3	14,1	13,0
Au	10,7	10,5	4,1	20,5	15,1	11,0	17,6
Cu	12,6	5,4	22,4	16,4	0,4	2,2	0,4
Zn	1,6	1,2	3,6	1,5		0,4	
Cd		4,7		5,8			

Table 4. Samples of non-precious alloys

	Ultratek	Victory	Wiron »S«	Wironit	Micronium
Ni	87,1	72,1	82,7		
Cr	12,5	23,2	16,9	26,6	27,1
Co	0,3			72,5	63,4
Fe	0,2	1,4	0,4	0,9	2,1
Nb		3,3			
Zr					7,4

Table 2 shows the results of a similar analysis performed on several samples of gold alloys manufactured in Yugoslavia.

Table 3 shows the results for several samples of Ag-Pd alloys which were analysed in the form of cubes for casting or sheets for crown rings.

Table 4 shows the results for several samples containing base metals, based on Ni-Cr and Co-Cr.

Table 5 shows the results for several alloys which were analysed both before and after melting. These results show the following characteristics:

1. Alloys for casting did not, after melting, reveal any significant changes in composition nor in the ratio of the fundamental components detected.

2. The values of fundamental components of Ag-Pd alloy sheets were reduced by half after melting. The mutual percentage ratio of elements in the main remain unchanged after melting even though the concentrations were reduced by half as a results of the presence of significant amounts of impurities, especially calcium.

3. The greater presence of iron after melting is a sign that the sample has been contaminated during laboratory manipulation (with metal forceps, etc.)

4. The greater presence of zinc on the sample surface after melting may be attributed to the fact that this element migrated to the surface in larger quantities in all samples where it was a component.

Table 5. Some samples of the alloys, analysed before and after melting

	Palador for casting		Auropal for casting		Gold alloy 20 carat		Palador plate		Auropal plate	
	before	after	before	after	before	after	before	after	before	after
Pd	11,2	9,9	15,2	11,6	0,1		14,1	6,5	18,3	9,3
Au	10,5	10,3	10,7	11,8	89,3	76,3	11,0	6,5	15,1	8,7
Cu	4,5	4,3	12,6	15,6	4,5	3,2	2,2	1,5	0,4	
Fe				0,7		1,7		3,5		3,3
Zn	1,2	4,4	1,6	16,3	0,6	2,2	0,4	4,9		6,2
Ca						10,3		42,7		37,0
Ag	67,0	66,9	59,9	44,0	5,5	6,3	72,3	34,4	66,2	35,5
Cd	4,7	4,2								

DISCUSSION

This method has the following advantages: 1.) it allows the analysis of a minimal sample surface (e. g. the cross section of a hair), 2.) the sample requires minimal preparation and is not destroyed during analysis, 3.) the sample can be of any size and shape and it can be in solid, liquid or gaseous state and 4.) simultaneous detection of macro and micro components is possible, with the limits of detection being 1 ppm or one part in 10^6 .

The method of X-ray emission spectroscopy may be applied in many disciplines: medicine, stomatology, biology, geology, fine arts, forensic science and especially as a means of identifying alloys and for quality control.

In this paper we have attempted to confirm the importance of this method for investigations in the field of fixed prosthodontics..

Since this method enables a precise quantitative and qualitative determination of elements in the analysed surface of a given object it provides the investigator with ideal and relative fast information (depending on the degree of training). For this reason it is advantageous in investigations of the composition of various sample surfaces and cross-sections, the structural homogeneity of the sample before and after processing, or before and after positioning it in the mouth.

The determination of the absolute chemical composition of the sample as a whole is limited for three fundamental reasons:

1. The composition of elements in a given target segment of sample surface is, in homogenous alloys but need not to be in non-homogenous ones, identical with the overall percentage composition and ratio of elements in the sample as a whole. In other words, the percentage ratio of elements determined for a given surface relates only to those elements found in that surface. This does not mean that the elements are present in the same ratios in the total quantity of alloy. As has already been said, this depends on the homogeneity of the sample.

2. The sample surface may become contaminated with unforeseen elements during manipulation or due to other chemical influences which must also be taken into consideration.

3. The strong signals of elements present in larger quantities can to some extent, mask the signals of elements with similar atomic numbers if they are present in much smaller quantities and create difficulties in the detection of the latter.

However the detection of elements in a given segment of the sample (outer surface of cross-section) can be regarded as the advantage of this method in our discipline, since, provided the percentage composition of the original homogenous alloy is known, it is possible to determine from the surface whether and to what degree the homogeneity of the alloy has been affected during laboratory processing. Furthermore, the fact that the sample is not destroyed is an advantage, not only because it preserves expensive materials and finished prostheses, but also because the experiment can be repeated in an unlimited number of times with the same sample. This, in turn, enables the multiple recording and allow the changes occurring on a given surface to be followed through time (without limit) to determinate the effects of various factors (chemical and electrochemical reactions and similar) and the effects of contamination within and outside of the oral cavity of the patient.

As shown by our results, some of these changes manifest as changes in the concentration of individual elements before and after melting, which indicates that the homogeneity of the alloy has been affected by the melting procedure.

CONCLUSION

The results of our studies on selected dental alloys indicate that X-ray emission spectroscopy is applicable and reliable as a complement to other well known methods for the investigation of dental alloys. Further application of this method should lead to significant discoveries.

Thus a quantitative and qualitative analysis of the composition of our materials, especially metal constructions for fixed prostheses, becomes more accessible. Since there is no necessity for destroying the sample repeated investigations are possible.

The method is fully qualitative and quantitative with regard to the analysed sample surface, but not for the total mass if the samples are not homogenous. This fact determines the specific applicability of this method.

Further investigations are in progress.

LITERATURE

1. NALLY J. N.: Chemico-Physical analysis and mechanical tests of the ceramo-metallic complex. *Int. Dent. J.* 18:309, 1968.
2. CIVJAN S., HUGET E. F., MARSDEN J. E.: Characteristics of two gold alloys used in fabrication of porcelain-fused-to-metal restorations. *J.A.D.A.* 85:309, 1972.
3. TRIFUNOVIĆ M. D.: Ispitivanje hemijskog sastava legura zlata u metalokermičkim sistemima. *Stom. Protetika* 1:12, 1981.
4. GREENER E. H., HARCOURT J. K. and LAUTENSCHLAGER E. P.: *Materials science in dentistry*, 1th ed, 112. Baltimore: The Williams and Wilkins Co, 1980.
5. CASTEL A. and VANDORPE B.: Analyse de l'or et de ses alliages par fluorescence et diffraction des rayons X. *Analisis* 7:282, 1979.
6. VALKOVIĆ V.: *Spektroskopija karakterističnih x-zraka*. Zagreb: Školska knjiga, 1980.
7. ANNEGARN H. J. et al.: PIXE Analysis of caries related trace elements in tooth enamel. *Nuclear Instruments and Methods* 181 North-Holland Publishing Co., 323, 1981.
8. CHAUDHRI M. A. and CRAWFORD A.: The influence of trace elements on fluoride uptake by teeth. *Nuclear Instruments and Methods* 181 North-Holland Publishing Co., 327, 1981.
9. CHAUDHRI M. A. and AINSWORTH T.: Applications of the PIXE to studies in dental and mental healths. *Nuclear Instruments and Methods* 181 North-Holland Publishers Co., 333, 1981.

Sažetak

IDENTIFIKACIJA KOMPONENATA PROTETSKIH SLITINA SPEKTROSKOPIJOM KARAKTERISTIČNIH X-ZRAKA

Poznavanje sastava protetskih slitina bitna je pretpostavka mogućnosti praćenja promjena u metalu koje nastaju obradom, kao i kasnije u odnosu s organizmom. Stoga je analiziran sastav nekih protetskih slitina s ciljem da se поближе upoznaju i ispituju mogućnosti metode u ovoj vrsti primjene. Rezultati su prikazani grafički i tablično. Prema razlikama u visini dobivenih vrhova i njihovim položajem može se zaključivati o koncentracijama i sastavu komponenata u ispitivanom uzorku. Prema tome, metoda je kvalitativna i kvantitativna te se može primijeniti i kod vrlo malih uzoraka i bez posebne pripreme. Uzorak se pri analizi ne uništava, što omogućuje opetovana ispitivanja. Pouzdani rezultati dobivaju se s površine uzorka. Na osnovu toga može se zaključivati o sastavu dentalnih slitina pod uvjetom da su homogene. Ovi fenomeni određuju specifičnost primjene ove metode, koja može vrlo dobro koristiti kao dopuna drugim poznatim metodama. Daljnja istraživanja su u tijeku.

Cljučne riječi: protetske slitine, sastav, identifikacija